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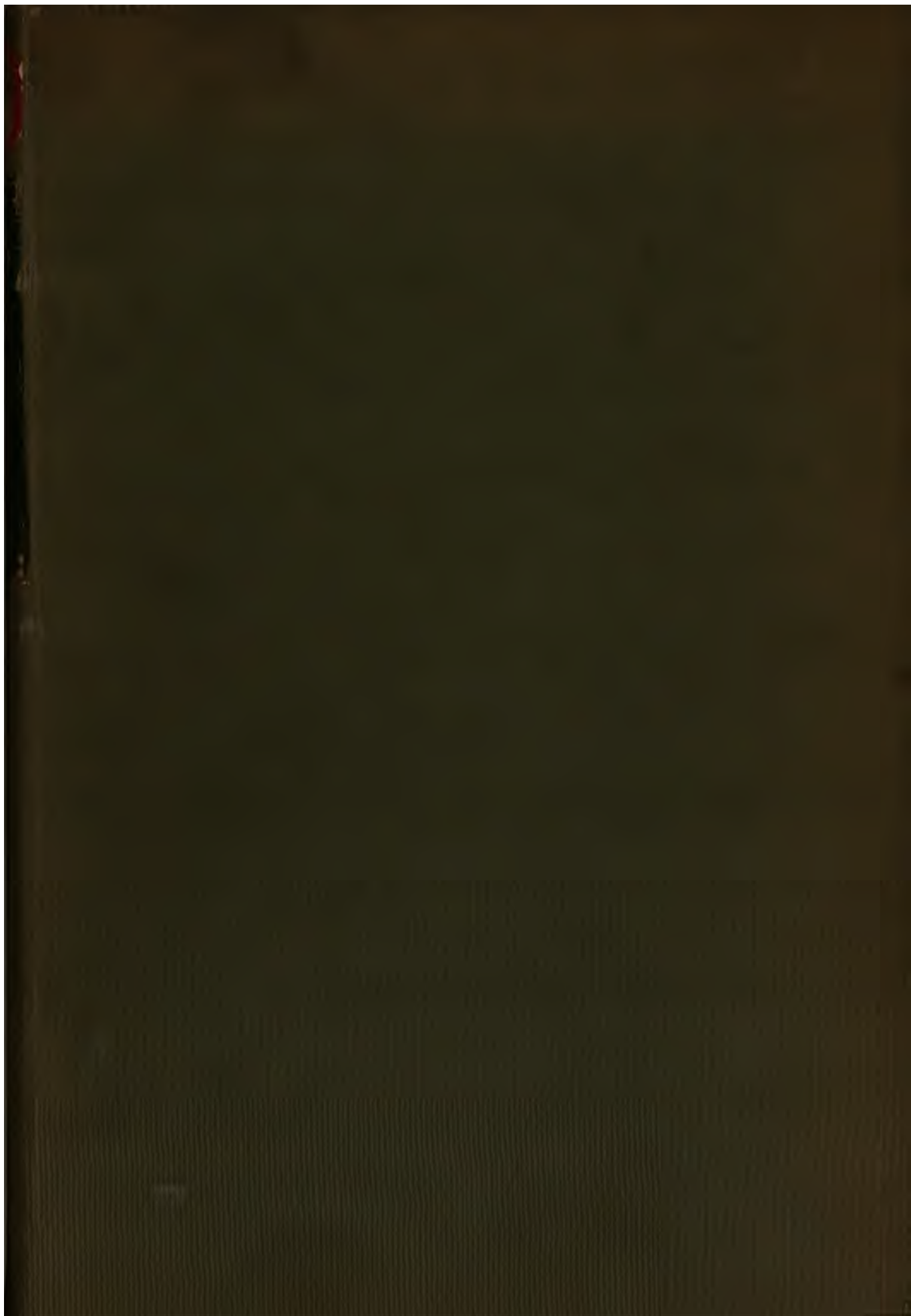
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**THE FREEZING-POINT LOWERING, CONDUCTIVITY, AND VIS-  
COSITY OF SOLUTIONS OF CERTAIN ELECTROLYTES  
IN WATER, METHYL ALCOHOL, ETHYL ALCOHOL,  
ACETONE, AND GLYCEROL, AND IN MIXTURES  
OF THESE SOLVENTS WITH ONE ANOTHER**

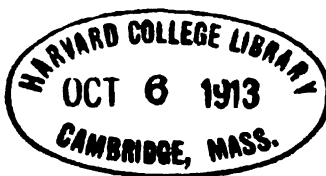
**By  
HARRY C. JONES AND COLLABORATORS**



**WASHINGTON, D. C.  
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## PREFACE.

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The work recorded in this monograph is supplementary to that in Publication No. 80 of the Carnegie Institution of Washington. Indeed, this is to be regarded as the second part of the above-named publication.

The experimental work herein described was carried out by Dr. C. M. Stine, Dr. J. N. Pearce, Dr. H. R. Kreider, Dr. E. G. Mahin, Dr. M. R. Schmidt, Dr. J. Sam Guy, and Dr. P. B. Davis. These gentlemen worked from one and a half to two and a half years each upon the problems in question, and the credit for these investigations is due primarily to them. The experimental work done by each is clearly indicated in the text.

This work has to do not only with the condition of the dissolved substances in the pure solvents referred to upon the title page, but, as is also implied in the title, in mixtures of these solvents with one another. Relations of interest, and it is hoped of value, especially between the conductivity of the dissolved electrolyte and the viscosity of the pure and mixed solvents, are brought out.

HARRY C. JONES.



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THE FREEZING-POINT LOWERING, CONDUCTIVITY, AND  
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WATER, METHYL ALCOHOL, ETHYL ALCOHOL, ACETONE  
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By

HARRY C. JONES AND COLLABORATORS.

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## INTRODUCTION.

Investigations in non-aqueous and mixed solvents have been continuously in progress in the Chemical Laboratory of Johns Hopkins University during the past twelve years. The results of the first seven investigations in this field have already been published as monograph No. 80, by the Carnegie Institution of Washington. The present monograph contains the results obtained in this field during the past six years, and it is to be regarded as the sequel to monograph No. 80.

A brief synopsis of some of the results obtained in the earlier work may not be out of place here, since it will serve to connect that work with the more recent, discussed in this volume.

The work of Jones and his cooperators comprises a uniform series of investigations, the same experimental methods being used in each. The conductivities were determined by the improved Kohlrausch method. The bridge wire, resistance boxes, thermometers, etc., were all calibrated or tested against the same standard instruments.

The conductivity water was purified by the method of Jones and Mackay,<sup>1</sup> and at 0° C. had a mean conductivity of  $1 \times 10^{-6}$ , and about twice that amount at 25°. The alcohols were purified by careful distillations, after being boiled with lime several times. The conductivity of the ethyl alcohol was between  $0.2 \times 10^{-6}$  and  $2 \times 10^{-6}$ , and that of the methyl alcohol was about the same as that of the water. The acetone was dried by calcium chloride, and had an average conductivity of about  $0.6 \times 10^{-6}$ .

Viscosity measurements were made by means of the modified Ostwald viscosimeter.<sup>2</sup> The work of Thorpe and Rodger<sup>3</sup> was consulted for the values of the viscosity of water at 0° and 25°.

The standard of conductivity is, in all cases, that of a fiftieth-normal solution of potassium chloride at 25°, which is taken as 129.7 reciprocal Siemen's units.

Jones and Lindsay undertook a further investigation of the phenomenon observed by Zelinsky and Krapin and by Cohen, namely, a minimum value of conductivity in a 50 per cent mixture of methyl alcohol and water. The solvents used were methyl, ethyl, and *n*-propyl alcohols, water, and binary mixtures of these liquids. The electrolytes studied were potassium, cadmium, and strontium iodides, ammonium bromide, and lithium nitrate. In every case it was found that the molecular conductivity of solutions in the mixed solvents was less than the average calculated from the conductivities in the components. In some cases, curves with well-defined minima were obtained at 0°, some of which persisted at 25°, while others developed into sagging curves with no minima. As a partial explanation of these facts, the following tentative suggestion was made:

It is known that water and the alcohols are highly associated substances; that is, their molecules in the liquid state exist as complexes, the composition of which varies with the temperature. According to the hypothesis of Dutoit and Aston, only those substances that are associated can appreciably dissociate molecules. Hence, water and the alcohols, on coming in contact, lower the state of association of one another

<sup>1</sup>Amer. Chem. Jour., 19, 91 (1897).    <sup>2</sup>Phys.-Chem. Mess., 2d ed., p. 260.    <sup>3</sup>Phil. Trans., 185, A, 307 (1894).



until a condition of equilibrium is reached. The mixture, being now less associated than its components, should have less dissociating power than the latter, and this is actually the case in every instance studied. Moreover, the lowering of conductivity is more marked when the alcohols are mixed with water than when they are mixed with each other, because they are associated to a less degree than water.

This conclusion was subsequently confirmed by Jones and Murray.<sup>1</sup> By means of cryoscopic measurements with water, formic and acetic acids, and mixtures of these liquids, they showed that the molecular weights of these substances were always less, even in very concentrated solutions, than the values obtained by Ramsay and Shields, who had found that these liquids are all highly associated in the pure condition.

Jones and Carroll<sup>2</sup> extended the work of Jones and Lindsay. The solvents used were water, methyl and ethyl alcohols, and various mixtures of these with one another. The electrolytes chosen were cadmium iodide, sodium iodide, calcium nitrate, hydrochloric acid, sodium acetate, and potassium iodide. Cadmium iodide in mixtures of methyl alcohol and water showed no minimum, except in the curves for  $V=16$ ,  $V=32$ , and  $V=64$  at  $0^\circ$ . Here a minimum appeared in the 75 per cent mixture. In all cases, however, the conductivities were less than the average values. In mixtures of ethyl alcohol and water, the same salt showed entirely similar phenomena, though no minima were observed. Sodium iodide gave a well-defined minimum in the 50 per cent mixture of methyl alcohol and water. Calcium nitrate in the same solvents gave no minimum, while the conductivities again did not obey the law of averages. Hydrochloric acid gave irregular results, but a minimum was noticed in a mixture containing 90 per cent methyl alcohol. Sodium acetate in various mixtures of acetic acid and water gave entirely irregular figures.

An effort was made to determine the dissociating power of the methyl alcohol-water mixtures, since it had been noticed that the molecular conductivity,  $\mu$ , for hydrochloric acid became constant at rather small dilutions in these solvents. Limiting values of conductivity were obtained for sodium, potassium, and ammonium iodides and bromides, and lithium nitrate, in 50 per cent methyl alcohol. In all these cases the dissociation was complete in the mixture at a dilution considerably less than that necessary for complete dissociation in water or methyl alcohol. It now remained to find the cause of the minimum.

Two factors are to be considered—amount of dissociation and ionic mobility. The first has been eliminated, hence the minimum must be caused by a decrease in ionic mobility. From the results of various observers, it was found that the viscosity of aqueous alcohol in the neighborhood of a 50 per cent mixture is higher than that of either of its constituents. Furthermore, the change in viscosity with increasing content of alcohol is more marked at lower temperatures than at higher, and rise in temperature shifts the maximum in viscosity, or minimum in fluidity, slightly towards the mixture containing the greater percentage of alcohol. These phenomena are closely paralleled by the conductivity minima. The latter all occur in or near the 50 per cent mixtures, and are more marked at  $0^\circ$  than at  $25^\circ$ . Cadmium iodide, for instance, shows a minimum at  $0^\circ$  in three solutions, but none at  $25^\circ$ .

<sup>1</sup>Amer. Chem. Journ., 30, 198 (1908).

<sup>2</sup>Id., 32, 531 (1904).

Potassium iodide, strontium iodide, and lithium nitrate give minima in the 50 per cent mixture at 0°, which move to the 75 per cent mixture at 25°.

A method was then devised for comparing the variations in fluidity and conductivity, and for studying the effect on conductivity of changes in fluidity. The differences between the (calculated) average values and the observed conductivities and fluidities in the various mixtures were expressed in percentages, and in all cases the variation in fluidity was found to be greater than the variation in conductivity.

Letting  $\Delta\phi$  and  $\Delta\mu$ , represent the two variations, then  $\frac{\Delta\phi - \Delta\mu}{\Delta\phi}$  represents the relative effect of variation in fluidity on conductivity. If the two effects are equal, the expression becomes equal to zero. It was found that in the 40 per cent mixtures the effect of change in fluidity on conductivity is greatest. Finally, the temperature coefficients of conductivity and of fluidity were not found to differ markedly; in other words,  $\frac{\mu}{\phi}$  is nearly a constant.

Jones and Carroll therefore conclude that the decrease in conductivity in binary mixtures is due primarily to a decrease in the fluidity of the solvent, and, consequently, a decrease in the ionic mobility, and secondarily to the effect of one associated solvent on the association of another.

A quantitative study of the relation between the conductivity and viscosity of different solutions was then made. In order that data for different solvents might be comparable, measurements were made with "comparable equivalent solutions," that is, solutions containing the same number of gram-molecules of electrolyte in the same number of gram-molecules of solvents. The result was that the conductivities of such solutions were found to be inversely proportional to the viscosity of the solvent, and directly proportional to the association factor of the solvent, or to the amount of dissociation of the electrolyte in that solvent. Otherwise expressed,

$$\frac{\mu\eta}{x} = \text{constant, or } \frac{\mu\eta}{a} = \text{constant.}$$

The work of Bassett<sup>1</sup> showed that silver nitrate, in mixtures of methyl alcohol and ethyl alcohol with water, presented phenomena entirely in accord with the observations of Jones and Lindsay and of Jones and Carroll. The conductivity curves for ethyl alcohol-water solutions fall far below the straight line of averages, but give no minima; the methyl alcohol-water curves, on the other hand, give well-marked minima at both 0° and 25°, the variation from the average being more pronounced at the lower temperature.

Jones and Bingham<sup>2</sup> introduced another solvent into the investigation, namely, *acetone*. The electrolytes studied were lithium nitrate, potassium iodide, and calcium nitrate, and quite unexpected results were obtained. Lithium nitrate, in mixtures of acetone and water, gave curves with an inflection-point at low dilutions and at 0°, which developed minima in the higher dilutions at 0°. The conductivity curves for solutions in mixtures of methyl and ethyl alcohols with acetone gave *maxima* which, in the higher dilutions, occurred always in the mixtures containing 75 per cent acetone. The curves are very nearly straight lines below this point, but

<sup>1</sup>Amer. Chem. Jour., 32, 409 (1904).

<sup>2</sup>Ibid., 34, 481 (1905).

drop rapidly to the values *in 100 per cent acetone*. This fact is important in connection with the work of Mahin, to be considered later. Potassium iodide in mixtures of the alcohols with acetone gave conductivity curves which were very nearly straight lines, either slightly convex or concave towards the axis, denoting percentages of acetone. In mixtures of acetone and water the same salt gave pronounced minima in the neighborhood of the 50 per cent mixtures. Calcium nitrate in mixtures of methyl and ethyl alcohols with acetone gave curves with maxima at both 0° and 25°. In mixtures with water the results were again irregular. In the first place, the values of  $\mu$ , for calcium nitrate in acetone are surprisingly small, less than those for lithium nitrate or potassium iodide, although it is a ternary electrolyte. In consequence, the curves for acetone-water mixtures, at dilutions greater than  $V=400$ , reach a minimum in the 50 per cent mixture, and rise to the 75 per cent mixtures—in this point resembling the curves for potassium iodide—but thereafter sink to the small values on the ordinate representing 100 per cent acetone.

The viscosity measurements brought to light the facts that the fluidity curves of mixtures of the alcohols with acetone are nearly straight lines, while the acetone-water mixtures give a minimum fluidity in the 50 per cent mixture. In general, therefore, the relation found by Jones and Carroll holds for mixtures containing acetone, that is, there exists a parallelism between the conductivity and fluidity curves. However, the maximum conductivity obtained with solutions of calcium and lithium nitrates in mixtures of acetone with the alcohols demands explanation. Two possible causes suggest themselves at once.

First, there may be an increase in dissociation in the 75 per cent mixtures, where the maximum occurs. Secondly, there may be an increased mobility of the ions, due to a diminution in the size of the ionic spheres. The idea of ionic spheres, proposed by Jones, postulates the existence of an atmosphere of solvent molecules clustered about the ion. To decide between these two possibilities, we may first consider the increase in dissociation. The fluidity data show that the acetone-alcohol mixtures are not more associated than the pure solvents; hence, using Dutoit and Aston's hypothesis, we should not expect to find greater dissociation in the mixtures. Moreover, while it is true that the maximum conductivity occurs in the 75 per cent mixture, this is true only for dilute solutions, the maximum shifting to the 25 per cent mixture as the concentration increases. This would not occur if the 75 per cent mixture had the greatest dissociating power. Therefore, the tentative view is accepted, that the maximum in conductivity is due to a change in the dimensions of the ionic spheres, and a consequent increase in migration velocity.

The conclusion of Dutoit and Friderich, and of Jones and Carroll, that conductivity is proportional to dissociation and inversely proportional to viscosity, must be supplemented by taking into consideration the possible changes in the size of the ionic spheres of solvent molecules.

Jones and Rouiller<sup>1</sup> undertook the study of silver nitrate. This salt gave results practically identical with those obtained by Jones and Bingham for lithium and calcium nitrates. The conductivity curves for acetone-water mixtures gave inflection-points in the higher concentrations and a pseudo-maximum in the 75 per

cent mixture, the value of the molecular conductivities declining rapidly, however, to the figures for pure acetone. The curves for mixtures of methyl and ethyl alcohols are nearly straight lines, following the fluidity curves; and maxima are found in the acetone-alcohol curves.

The investigation was extended by McMaster<sup>1</sup> to a study of lithium bromide and cobalt chloride. The former behaved normally in all the mixtures of the alcohols and water; that is to say, a minimum was noticed in the conductivity curves at 0° and 25° in mixtures of the alcohols with water, while the results for mixtures of the two alcohols obeyed the law of averages almost exactly. In mixtures containing acetone, relations were found very closely analogous to those obtained by Bingham in the case of lithium nitrate. The solutions in alcohol-acetone gave maxima of conductivity in the 75 per cent acetone mixture; while the solutions in water gave minima at the higher dilutions and inflection points at the lower dilutions. The unusual behavior of the acetone mixtures is here again very evident.

Cobalt chloride, on the other hand, gave unexpected results. In the first place, the conductivity of its solutions in ethyl alcohol is surprisingly low, being only about 15 per cent as great as in water. In mixtures of ethyl alcohol and water, cobalt chloride gave an inflection point in nearly all the solutions, but in the curves for  $V=200$  to  $V=1,600$ , at 0°, the value of  $\mu$ , is greater in the 75 per cent than in the 50 per cent mixture, thereafter declining to the lower values in pure ethyl alcohol. Exactly the same phenomenon is shown by calcium nitrate in acetone-water solutions, where the curves rise from the 50 per cent to the 75 per cent mixture, and drop off rapidly in pure acetone. Rouiller found similar results for silver nitrate. In solutions of methyl alcohol and water, cobalt chloride is normal, giving pronounced minima in the 50 or 75 per cent mixtures. Methyl alcohol-ethyl alcohol solutions gave nearly straight lines, as did also solutions in acetone-methyl alcohol. In the last cases the fluidity curves are also nearly straight lines, but the acetone-methyl alcohol conductivity curves have a slope which is the reverse of the fluidity curve. Acetone and ethyl alcohol gave a maximum in the 25 per cent mixture.

In most of the above cases we see that the conductivity varies directly as the fluidity, and fluidity minima are usually accompanied by conductivity minima. The converse, that conductivity minima were accompanied by fluidity minima, was not always found to be true, as, for instance, with cobalt chloride in acetone-ethyl alcohol. Here a maximum of conductivity is found in mixtures giving a fluidity curve which differs by less than experimental error from a straight line. Again, the conductivity curves for acetone-water show inflection-points, while the fluidity curve has a minimum. These apparently irregular results are to be considered again in the work of Jones and Mahin.

In explanation of the minimum of conductivity, Jones and McMaster adopt the view that the diminution in the fluidity of the solvent is an important factor in determining the conductivity minimum. But this does not account entirely for the phenomenon. The change in the size of the ionic sphere, the atmosphere surrounding the ion, must also be considered. The velocity of the ion depends not only on its composition, but also on its attraction for the solvent.

<sup>1</sup>Amer. Chem. Journ., 36, 325 (1906).

There yet remain for consideration the several maxima of conductivity noticed in this work as well as in that of Bingham. The discussion of the latter work has shown that it is improbable that the maxima are due to an increase in dissociating power in the mixture where they occur. Moreover, an examination of the conductivities of lithium bromide and cobalt chloride shows that complete dissociation is more nearly reached in the pure solvents than in the mixtures where the maxima are found. Hence, it was concluded that the cause of the effect is primarily a change in the dimensions of the ionic spheres.

Some points of interest were noted in connection with the temperature coefficients of conductivity and of fluidity. First, in nearly every case the temperature coefficients of conductivity are greater in the more dilute than in the more concentrated solutions. The work of Jones has shown that in practically all solutions there is some combination between solvent and solute, and that the solvates become more complex as the dilution increases. Therefore, change in temperature, which affects the complex solvates most, has a greater effect on the conductivity of the more dilute solutions.

A second point worth noting was that in certain solutions negative temperature coefficients of conductivity were found. These manifested themselves in solutions of cobalt chloride in acetone, in 75 per cent acetone and methyl alcohol, and in 50 and 75 per cent acetone and ethyl alcohol. In the 75 per cent acetone and methyl alcohol, when  $V=200$ , the temperature coefficient is *zero*.

The change in conductivity with temperature is the algebraic sum of two opposing influences. First, rise in temperature diminishes dissociation; second, rise in temperature is accompanied by an increase in fluidity. The first of the processes tends to decrease conductivity, the second to increase it. When the sum is positive we have increasing conductivity with rise in temperature, as is usually found to be the case. In the one instance mentioned above the two forces are equal, and the conductivity is independent of the temperature.

The investigation of Jones and Veazey<sup>1</sup> included a study of the behavior of copper chloride and potassium sulphocyanate. Both of these electrolytes gave results which were almost entirely "normal;" that is, conductivity curves followed fluidity curves in every case except two. These exceptions were the curves for copper chloride in mixtures of the alcohols with water. No minima were found here corresponding to the well-marked minimum in fluidity, although the conductivities were always less than required by the law of averages. An inflection-point occurs between the 50 and 75 per cent mixtures. The conductivity curves of potassium sulphocyanate show no such irregularity, but are in every respect parallel to the fluidity curves of the solvents.

In addition to determining the fluidities of the various solvent mixtures, Jones and Veazey measured the fluidities of solutions of potassium sulphocyanate in these mixtures. It was found that in many cases the fluidity of the solution is greater than the fluidity of the solvent; in other words, potassium sulphocyanate, under certain conditions, has a negative viscosity coefficient. In mixtures of methyl alcohol and water the viscosity of the tenth-normal solutions is less than that of the 0, 25, and 50 per cent solvent mixtures and greater than the 75 per cent mixture, becoming

<sup>1</sup>Amer. Chem. Journ., 37, 405 (1907); Zeit. phys. Chem., 61, 641 (1908).

equal at some point corresponding to about 65 per cent alcohol. The same phenomena repeat themselves in mixtures of ethyl alcohol and water. With acetone and water the negative viscosity coefficient again becomes apparent, this time only in the 0 and 25 per cent mixtures. In the other mixed solvents the viscosity is increased by the addition of the solute.

An examination of the literature relating to viscosity brought to light the important fact that, in general, only salts of potassium, rubidium, and caesium are known to lower the viscosity of water. Very few other cases of negative viscosity have been found, and not all salts of these metals behave alike in this respect. For instance, the sulphate, ferrocyanide, ferricyanide, and chromate of potassium give positive viscosity coefficients. And it is not remarkable that, in the presence of certain anions, the alkali cations do not give negative viscosity coefficients. Viscosity must be considered to be a property which is a function of the nature of all the particles in a solution; and it is perfectly clear that here, as in conductivity, two opposing influences may be operative, the potassium cation, for instance, tending to lower the viscosity and the anion tending to increase it. If the algebraic sum is positive, a positive viscosity results, and *vice versa*, the actual viscosity of the solution being dependent on the relative action of the two ions.

The facts have been presented showing that in aqueous solution, or in solutions containing as much as 50 per cent of water, potassium sulphocyanate produces a lowering of the viscosity. What is the mechanism of this effect?

The work of Thorpe and Rodger<sup>1</sup> has shown that viscosity phenomena are, in all probability, dependent upon the frictional surfaces of the various particles in any solution. If the total frictional surface can be diminished by any means, other factors remaining constant, the viscosity will be lowered. We may actually realize this by bringing into a solvent a substance which has a large molecular volume, or which gives ions having large ionic volumes. The total frictional surface proportional to the mass is thus lessened, since the surface increases as the square of the diameter of the particles, while the mass increases as the cube. Potassium, rubidium, and caesium salts, as we have said, lower the viscosity of water. Are their atomic volumes, accordingly, larger than those of other elements? The periodic curve of atomic volumes answers this question at once. The alkali metals occupy the maxima of the curve, and no other metals have atomic volumes to be compared with them. Moreover, that element having the greatest atomic volume—caesium—should have the greatest negative viscosity coefficient. This point is soon tested by reference to the work of Wagner.<sup>2</sup> If the viscosity of water is taken as unity, a normal solution of caesium chloride lowers it to 0.9775, a normal solution of rubidium chloride gives 0.9846, and potassium chloride 0.9872. Thus, the effect on viscosity varies directly as the atomic volume of the cation; caesium having an atomic volume of 74, rubidium of 57, and potassium of 47.

It will be remembered that minima of fluidity were found in mixtures of water with the alcohols or with acetone, accompanied usually by minima in conductivity. The fact also came out that in those mixtures which have the minimum fluidity, the temperature coefficients of conductivity are largest. The explanation of this

<sup>1</sup>Zeit. phys. Chem., 14, 361 (1894); 19, 323 (1896).

<sup>2</sup>Ibid., 5, 35 (1890).

is sufficiently evident. Each solvent, highly associated in the pure condition, breaks down the association of the other, as shown by Jones and Murray, so that the resulting mixture is composed of a greater number of smaller molecules in a given volume. Simple molecules would probably have greater chemical activity than the more complex ones, and would combine with the solute to a greater extent. The effect of heat on such solvates would be greater with increasing complexity of the solvate. In connection with this breaking down of the solvents into simpler aggregates, the total internal frictional surface would be increased, and an increase in viscosity is the result. Again, in terms of Dutoit and Aston's hypothesis, the dissociating power of such a mixture should be less than that of the pure solvents, and this is an important factor in determining the conductivity minimum, as pointed out by Jones and Bingham. It is noticed that in these mixtures of minimum fluidity there is a smaller increase of conductivity with dilution than in the other mixtures, and this is, of course, a consequence of the view here adopted.

In a second communication,<sup>1</sup> Jones and Veazey took up a study of solutions of tetraethylammonium iodide—Walden's "Normalelektrolyt"—in mixtures of water, the alcohols, and nitrobenzene. The latter is a solvent of a type entirely different from the hydroxy-compounds or acetone, and it was important to know whether the relations previously found would hold for mixtures containing this substance.

In mixtures of both the alcohols with water, tetraethylammonium iodide shows a well-defined conductivity minimum in the neighborhood of the 50 or 75 per cent mixtures at both 0° and 25°. In mixtures of the alcohols with each other, no minima appeared, although the values are less than the averages. Mixtures of methyl alcohol and nitrobenzene behaved similarly, but mixtures of ethyl alcohol and nitrobenzene gave a maximum in the solutions containing 25 per cent of the latter. The fluidity curves of mixtures of water and the alcohols have already been sufficiently treated, and here, as before, the conductivity curves follow them closely. The same general relations appear in mixtures of nitrobenzene and the alcohols. A fluidity maximum shows itself in mixtures containing 25 per cent of nitrobenzene, with either alcohol, and at 0° and 25°. Hence, the conductivity curves, in the case of nitrobenzene-ethyl alcohol mixtures at least, follow the fluidity curves, and the variation with nitrobenzene-methyl alcohol is slight.

It has now been shown that for all the solvents worked with, it is practically a constant phenomenon for conductivity curves to have the same general characteristics as fluidity curves. On the other hand, we must not lose sight of the fact that several well-marked exceptions have been found, and notably in mixtures containing acetone. Here the fluidity curves for water-acetone have minima, and for acetone-alcohol are nearly straight lines, while the conductivity curves for lithium bromide, lithium nitrate, cobalt chloride, and calcium nitrate show pronounced maxima, or pseudomaxima. Moreover, the values of the molecular conductivities in acetone are abnormally low, except for lithium salts.

In the work of Walden,<sup>2</sup> already referred to, it was found that the product of the limiting molecular conductivity of tetraethylammonium iodide and the viscosity of its infinitely dilute solutions is nearly a constant for about thirty organic solvents

<sup>1</sup>*Zeit. phys. Chem.*, 62, 41 (1906).

<sup>2</sup>*Ibid.*, 55, 207 (1906).

and equal to about 0.7. Water and glycol are exceptions, giving products equal to 1.0 and 1.32, respectively. The product  $\mu_{\infty}\eta$  is also independent of temperature. Therefore, generally speaking, conductivity varies as the fluidity of the solvent. But, as we have shown, in certain solutions containing acetone this relation no longer holds.

It may further be noted that Jones has shown<sup>1</sup> that cadmium iodide and ammonium sulphocyanate, in acetone solutions, have abnormally high molecular weights, although such solutions conduct the current. He pointed out that these facts indicate simultaneous association and dissociation of the solute; a high concentration of molecular complexes, which causes an abnormal apparent molecular weight, co-existing with a low ionic concentration, which causes a low conductivity value. A consideration of these points suggested to Jones and Mahin<sup>2</sup> several lines of inquiry, which were taken up by them. They sought to answer the following questions:

1. Will those salts that have, at ordinary concentration, abnormally low values for molecular conductivity, possess, when completely dissociated, values which are inversely proportional to the coefficient of viscosity?
2. If so, is the product of molecular conductivity and viscosity constant for mixed solvents and at different temperatures?
3. Is the value of the constant the same for different electrolytes?
4. Are the abnormal conductivities in acetone and mixtures of acetone with other solvents due to association of the salt?

The first salt studied was lithium nitrate. Extreme precautions were taken to insure purity of the solvents, and measurements were carried to dilutions as high as 200,000 liters wherever practicable. Under these conditions the conductivity curves assumed forms which differed markedly from those obtained for dilutions between 10 and 1,600 liters, and which closely resembled the fluidity curves. Moreover, the product of the viscosity coefficient and the maximum conductivity in solutions of acetone mixed with the alcohols has a mean value of 0.62, agreeing well with Walden's value of 0.70 for simple solvents, and being independent of temperature. With acetone-water mixtures, the product varies between 1.00, the value for water, and 0.63, the value for acetone.

Some determinations of the molecular weight of lithium nitrate in acetone by the boiling-point method brought out interesting results. The concentration of the solutions varied roughly between normal and tenth-normal. Even in the more dilute solutions the indicated molecular weight was 83.1, while the value required by the formula  $\text{LiNO}_3$  is 69.07. This accounts for the low conductivity of lithium nitrate in acetone solutions of not very great dilution.

As already stated, cadmium iodide was found by Jones to be associated in acetone, and a study of this salt was next made. Results in this case were not so satisfactory as with lithium nitrate. The conductivity curves show signs of regaining a similarity to the fluidity curves, but the resemblance is not so close as with the other salt. Moreover, the product of the viscosity by the maximum conductivity is irregular. The conductivity data show that in most cases a limiting value was not reached with cadmium iodide, and some solutions more nearly approached the true

<sup>1</sup>Amer. Chem. Journ., 27, 16 (1905).

<sup>2</sup>See "Work of Mahin" in this monograph.



values than others, thus causing the fluctuations in the value of the product. It must be borne in mind that conductivity measurements at dilutions so great (400,000 liters) that the correction for the conductivity of the solvent often amounts to more than 50 per cent of the total, are being made at a point where the method is taxed rather beyond its limitations; and it is not surprising that, even with the utmost precautions, concordant results were not obtained. The failure of cadmium iodide to follow the behavior of lithium nitrate in very dilute solutions is merely negative evidence, and must be weighed as such.

Some boiling-point determinations of cadmium iodide in acetone were made, and here, too, considerable polymerization was found. In a 0.09 normal solution the indicated molecular weight was 448, calculated 364.

Thus, the apparent exceptions to the relations found by Jones and his coworkers are seen to vanish when we are dealing with what are practically infinitely dilute solutions. The investigations have dealt with twelve electrolytes and six solvents, and in every instance the same relations were found to hold, connecting the molecular conductivity with the fluidity.

Jones and Mahin<sup>1</sup> also made a study of the conductivity and viscosity of lithium nitrate in ternary mixtures of the four solvents used above. The results were about what would be expected from a knowledge of the solutions in binary mixtures. The conductivity curves, in the great majority of cases, followed the fluidity curves, and no new relations were brought to light.

As a result of this work, we may make the general statement: If we mix methyl and ethyl alcohols, or methyl alcohol and acetone, the conductivity curves are very close to straight lines, and the fluidities of the mixture are nearly additive. Take, for instance, the last case mentioned. Table 1 shows the fluidities of various mixtures of methyl alcohol with acetone at 0°, as determined by the viscosimeter, and also as calculated from those of the two components.

TABLE 1.—*Fluidity of Mixtures of Methyl Alcohol and Acetone at 0°.*

	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
Fluidity observed....	122.2	153.9	187.4	222.2	244.1
Fluidity calculated...	.....	152.7	183.2	213.7	.....

The observed fluidities are very nearly the averages corresponding to the different mixtures. On the other hand, if we mix water with the alcohols, or with acetone, there is interaction between the components of the mixture; and certain of its physical properties are found no longer to bear simple relations to the properties of the single solvents. Otherwise expressed, the law of averages is not followed, and the properties of the mixture are not additive. Hence, we may conclude that water, mixed with the other three solvents, causes some deep-seated change in the state of molecular aggregation of the liquid molecules, while mixing the three organic solvents with each other causes no such change. The various mixed solvents may therefore be divided into two classes, those not containing water with properties nearly or quite additive, and those containing water with properties that are not the averages of the two components.

<sup>1</sup>Amer. Chem. Jour., 41, 433 (1909).

## WORK OF C. M. STINE.

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Six independent lines of evidence, all pointing to the existence of hydrates in aqueous solutions, having been established, it seemed desirable to attempt to determine, if possible, the effect of one salt with hydrating power on the hydrates formed by a second salt in the same solution; also the effect of a salt with very small hydrating power on the hydrates formed by another salt. When both salts possess the power of forming hydrates in single solution, the amounts of water taken up by the salts at the same concentrations may be the same, or may vary within wide limits. We proposed to study binary mixtures in which both conditions are illustrated.

Since we desired to calculate, as accurately as possible, the approximate composition of the hydrates formed in the mixtures, it was necessary to obtain data for the freezing-points, conductivities, and number of grams of solvent in a liter of solution of the various salts employed. In order that we might have the data for the exact normalities of the solutions which we mixed, it seemed advisable to make the necessary measurements in the single solutions, rather than to attempt to interpolate from data previously obtained.

### CONDUCTIVITY CALCULATIONS.

It is well known that when two or more electrolytes are present in the same solution, the conductivity of this solution is not, in general, equal to the sum of the conductivities which these electrolytes show in separate solutions of the same normality as that which these salts may be assumed to have in the mixture; but that the conductivity of the mixture is generally less than this sum. If the solutions are isohydric,<sup>1</sup> that is, if the component solutions possess a common ion in equal concentration, then the simplest condition exists between the conductivities of the single solutions and that of the mixture. This latter condition exists when

$$\frac{a_1}{v_1} = \frac{a_2}{v_2}$$

in which  $a_1$  is the dissociation of one of the electrolytes at the dilution  $v_1$ , and  $a_2$  is the dissociation of the other electrolyte at the dilution  $v_2$ . Such solutions can be mixed in any proportion without altering their dissociation, and hence the conductivity of the mixture is the mean of the conductivities of the component solutions and can, therefore, be calculated according to the equation

$$k = \frac{k_1 P + k_2 P'}{P + P'}$$

in which  $k_1$  and  $k_2$  are the conductivities, and  $P$  and  $P'$  the proportions of the component solutions.

Unfortunately, we have to deal with no such simple relations as these in the mixtures with which we worked. In our work the viscosity of the mixtures differs

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<sup>1</sup>Arrhenius: *Wied. Ann.*, **30**, 51 (1887); *Zeit. phys. Chem.*, **2**, 284 (1888).

considerably, in many cases, from that of the single solutions assumed to have the same normality. This would involve changes in friction in the movement of the ions. Also, the amount of water combined as hydrate, *i. e.*, the dimensions of the atmosphere about the ion, continually changed from one normality to another. This involved a varying degree of freedom of movement of the ions. Again, the variation in the number of particles present, ions and molecules, must involve continual variation in the amount of friction between the ions. As a comparatively short, and at the same time sufficiently accurate method, we have adopted the following in apportioning the diminution in conductivity to the constituent salts: Since we have dealt in every case with mixtures in which the two electrolytes have a common ion, we have based the method on the number of this common ion yielded by the constituent salts in separate solutions at the same normality. By the same normality we mean that if equal volumes of two solutions are mixed, and any diminution in volume which may take place upon mixing is compensated for by the addition of pure solvent, then the normality of each solution in the mixture may be assumed to be exactly half of that of the constituent solutions. If suppression of the ionization is dependent upon the common ion, then it will be inversely as the number of this common ion furnished by each of the salts in a mixture. This number was obtained thus: The figure representing the normality of the individual solutions, multiplied by the value of  $\alpha$  for the solution at the normality in question, would give the gram-atomic weight of the common ion. Suppose the case to be one where a solution of potassium chloride has been added to an equal volume of a solution of calcium chloride. It being assumed that calcium chloride dissociates into  $\text{Ca}^{++}$  and  $\text{Cl}^-$ , the figure representing the gram-atomic weight of the common ion would have to be doubled for a ternary electrolyte, such as calcium chloride. Since two chlorine ions are required to re-form a molecule of calcium chloride, the figure expressing the number of chlorine ions driven back, in the case of calcium chloride, must be divided by two, in order to get the relative number of molecules of calcium chloride re-formed.

Let us take the values of  $\mu_\infty$  as expressing the molecular conductivity of the completely dissociated molecules of the various salts. If the figures for the relative numbers of molecules of the two salts re-formed be multiplied by the proper value of  $\mu_\infty$ , we shall then have the relative losses in conductivity. From this the absolute losses are readily obtained. An example may suffice to make this clear: Take the case of the mixture of equal volumes of a solution of 1.8 N calcium chloride and of 1.7 N potassium chloride. The resulting solution, any diminution of volume having been compensated for, will consist of 0.9 N calcium chloride and 0.85 N potassium chloride. The dissociation of a 0.9 N solution of the specimen of calcium chloride employed was found, by conductivity measurements, to be 53.2 per cent; of 0.85 N potassium chloride, 8.32 per cent. Doubling the value of  $\alpha$  in the case of calcium chloride and multiplying by the normality, we get 0.9576. Similarly, for potassium chloride, 0.7068. These represent the relative numbers of chlorine ions which would be furnished by each salt in the mixture if no suppression of the ionization took place upon mixing. That is, if driving back occurs, according to the law of

mass action, 707 chlorine ions should be driven back to re-form calcium chloride to 958 for potassium chloride. But since it requires two ions of chlorine to re-form each molecule of calcium chloride, only 354 molecules of calcium chloride will be re-formed to every 958 molecules of potassium chloride. Multiplying these values by  $\mu_{\infty}$  for calcium chloride and potassium chloride, respectively, we get 5,222, approximately, for calcium chloride and 7,695 for potassium chloride. These values represent the relative losses in conductivity upon mixing. From this the decrease in conductivity can be apportioned between the two salts.

All conductivity measurements are given as specific conductivities in the mixtures. The units employed are reciprocal centimeter-ohms. For purposes of comparison with the previous work upon the "hydrate theory" our units may be transformed by dividing  $\mu$ , by 1.069.

The approximate composition of the hydrates in the *single* solutions was calculated by the method previously employed by Jones and his coworkers.

#### EXPERIMENTAL WORK.

*Freezing-point.*—The more concentrated solutions were frozen by means of a mixture of solid carbon dioxide and alcohol, the freezing temperature being determined by means of alcohol thermometers. These temperatures could not be measured more closely than 0.5°. For the more dilute solutions freezing-mixtures of ice and sodium chloride, or ice and crystallized calcium chloride, were employed. The temperature was read by means of Beckmann thermometers, covering ranges of 6°, 12°, and 25°, respectively. When the more concentrated solutions were frozen they were removed from the bath of solid carbon dioxide and alcohol as soon as ice began to separate, in order that they might not be surrounded by the very cold freezing-mixture while temperature equilibrium was being established. The necessary correction for the separation of ice and consequent increase in concentration was introduced in every instance. The separation of some of the dissolved substance was readily ascertained by the grit or sand-like character of the solid that separated, which was easily detected. Since it was found that, for the volume of liquid employed in the freezing-point tube (about 25 c.c.), a freezing-point determination made with a large undercooling and, consequently, a copious separation of ice, gave a slightly different result from one where the undercooling was less; care being taken, in the freezing-point determinations of both the pure solvent and the solutions, to keep the undercooling nearly the same throughout—about a degree. This necessitated inoculating the solution, in nearly every case, with an exceedingly minute particle of the solid phase of the solvent.

#### CONDUCTIVITY.

Conductivities were measured by the method of Kohlrausch.

The resistance coils, manufactured by Leeds & Co., were tested and found in no case to involve a greater error than 0.04 per cent.

The dilute solutions were measured in conductivity cells of the form employed by Jones and Bingham,<sup>1</sup> the tubes carrying the platinum electrodes being sealed

<sup>1</sup>Amer. Chem. Journ., 34, 481 (1906).

into both the upper and lower walls of the stopper. For the more concentrated solutions, cells of the type used by Jones and Getman<sup>1</sup> were employed. The electrodes were treated in the usual manner (coated with platinum black, etc.), in order to obtain a sharper tone minimum or point of silence in the readings.

The cells for the more dilute solutions were standardized by determining the cell constant by means of N/50 potassium chloride. The value  $k=0.0015133$  was taken as the conductivity of N/50 potassium chloride. For the more concentrated solutions the cell constants were determined with a N/2 solution of potassium chloride, for which  $k=0.03365$  at  $0^\circ$ .<sup>2</sup> The potassium chloride employed in determining cell constants was recrystallized five times, the last two times from conductivity water, and was free from all appreciable impurities. The cell constants were frequently redetermined, but very little change in them was noted from time to time. The cells were filled with distilled water when not in use, and were always carefully cleansed, dried, and rinsed with the new solution when a change in solutions was made. All conductivities were measured at  $0^\circ$  C. The temperature of the zero bath was always within a tenth of a degree of  $0^\circ$  C., as determined by an accurately standardized thermometer. All conductivity measurements are the average of four readings with different resistances in circuit.

The water used in this work was purified as in former work.

It is well known that the conductivity method is not an accurate measure of dissociation in concentrated solutions. Especially is this the case at the concentrations with which we dealt, since the values of  $\mu_\infty$ , which we used in our mixtures, were determined for each salt by diluting the single solution to a maximum value of  $\mu_\infty$ . This is, obviously, a source of additional error, for the conductivity of the ions resulting from a completely dissociated molecule in a very dilute solution must be different from the conductivity of those ions in a more concentrated solution. In the more dilute solution a larger atmosphere of the solvent is attached to the ions, and this must be dragged along by them. There is present a much smaller number of particles of salt (ions or molecules) in the dilute than in the more concentrated solution. Consequently, the friction between the ions in their movements must be different. The viscosity of the solutions in which  $\mu_\infty$  can be determined is very much less than the viscosity of the solutions at the concentrations employed. These are all important factors which affect the conductivity of any dissolved substance. The method is, however, an approximate one for measuring such dissociations, and is the best available at present. All that can be said is that it probably gives values of the right order of magnitude.

#### CALCIUM CHLORIDE.

A strong solution of calcium chloride was prepared and standardized. All solutions were made by diluting the calculated amount of the original solution to the required volume. Table 2 gives the data as to freezing-point measurements, conductivity measurements, weight-normal corrections (or number of grams of solvent in 1,000 c.c. of solution), and hydrates.

<sup>1</sup>Zeit. phys. Chem., 46, 354 (1903).

<sup>2</sup>These values are calculated from the results of Jones and West. See Amer. Chem. Journ., 34, 381 (1906).

In the tables of this volume the following symbols are used:

- $m$  = concentration in terms of gram-molecules per liter;  
 $\Delta$  = observed freezing-point lowering corrected for separation of ice;  
 $\Delta/m$  = molecular lowering of freezing-point;  
 $V$  = number of letters that contain a gram-molecule of the dissolved substance;  
 $k$  = specific conductivity;  
 $\mu_0$  = molecular conductivity at  $0^\circ = 1,000 \times V \times k$ ;  
 $\alpha$  = percentage of dissociation  $= \mu_0 / \mu_\infty$ ;  
 $W_{\text{sol}}$  = weight of 25 or of 50 c.c. or of a smaller volume of the solution;  
 $W_{\text{salt}}$  = weight of salt contained in this volume of the solution;  
 $W_{H_2O}$  = weight of water in this volume of solution  $= W_{\text{sol}} - W_{\text{salt}}$ ;  
 Correction per cent = percentage of correction to be applied in order to refer measurements to 1,000 grams of solvent;<sup>1</sup>  
 $L$  = theoretical molecular lowering of freezing-point referred to 1,000 grams of the solvent;  
 $P$  = parts by volume of each of the solutions = 1, unless otherwise stated;  
 $L'$  = corrected molecular lowering;  
 $M$  = number of gram-molecules of water in combination, both being referred to 1,000 grams of solvent;  
 $H$  = number of molecules of water in combination with one molecule of the salt, at the concentration in question.

TABLE 2.—Data of Freezing-point, Hydrates, Conductivity, and Weight-normal Corrections of Calcium Chloride.

Freezing-point.			Hydrates.				
$m$	$\Delta$	$\Delta/m$	$\alpha$	$L$	$L'$	$M$	$H$
0.3	1.517	5.056	0.634	4.22	5.02	8.8	29.4
0.5	2.672	5.344	0.594	4.09	5.29	12.6	25.2
0.6	3.270	1.755	0.568	3.97	5.39	14.6	24.3
0.7	4.065	5.807	0.557	3.93	5.72	17.4	24.8
0.9	5.422	6.024	0.532	3.84	5.90	19.4	21.6
1.0	6.410	6.310	0.512	3.76	6.16	21.6	21.6
1.1	7.080	6.436	0.502	3.73	6.26	22.4	20.4
1.35	9.362	6.934	0.466	3.59	6.72	25.9	19.2
1.4	10.05	7.18	0.455	3.55	6.94	27.2	19.4
1.55	11.58	7.47	0.434	3.47	7.18	28.7	18.5
1.75	14.33	8.16	0.414	3.40	7.83	31.4	17.9
1.8	14.69	8.16	0.405	3.37	7.80	31.6	17.5
2.2	21.07	9.58	0.357	3.19	9.03	35.9	16.3
2.7	30.25	11.20	0.296	2.96	10.39	39.7	14.7
3.1	39.5	12.74	0.250	2.79	11.65	43.6	14.1
3.51	49.5	14.10	0.207	2.63	12.68	46.5	13.2

<sup>1</sup>These are not specific gravity measurements made in pycnometers, and the correction percentage is therefore given only to the first decimal.

TABLE 2—Continued.

Conductivity.				Weight-normal corrections.			
<i>m</i>	<i>V</i>	<i>k</i>	$\mu_s$	<i>W<sub>sol</sub></i>	<i>W<sub>salt</sub></i>	<i>W<sub>H<sub>2</sub>O</sub></i>	Correction, per cent.
0.3	3.333	0.02804	93.5	51.270	1.665	49.505	0.8
0.5	2.000	0.04380	87.6	52.2608	2.775	49.4858	1.0
0.6	1.6666	0.05027	83.8	52.7437	3.33	49.4137	1.2
0.7	1.4285	0.05755	82.2	53.1162	3.885	49.2312	1.5
0.9	1.1111	0.07060	78.4	53.9816	4.995	48.9866	2.0
1.0	1.000	0.07554	75.5	54.326	5.55	48.776	2.4
1.1	0.909	0.08157	74.1	54.772	6.105	48.667	2.7
1.35	0.7407	0.09286	68.8	55.9435	7.4925	48.451	3.1
1.4	0.7143	0.09396	67.1	56.115	7.770	48.345	3.3
1.55	0.6453	0.09918	64.0	55.6562	8.6025	48.0537	3.9
1.75	0.5698	0.10723	61.1	57.7040	9.7402	47.9638	4.1
1.8	0.5555	0.10727	59.8	28.900	4.995	23.905	4.4
2.2	0.4545	0.11588	52.7	29.650	6.105	23.545	5.8
3.7	0.3704	0.7757	43.6	30.682	7.492	23.190	7.2
3.1	0.3226	0.11410	36.8	31.461	8.602	22.859	8.6
3.51	0.2849	0.10710	30.5	32.187	9.720	22.467	10.1

## POTASSIUM CHLORIDE.

In order to investigate the effect of the presence of a salt with little hydrating power on a salt with considerable hydrating power, potassium chloride was added to calcium chloride. The data for the various solutions of potassium chloride alone are given in table 3. There is evidently no hydrating power.

TABLE 3.—Data for Potassium Chloride, giving Freezing-point and Conductivity Measurements, Weight-normal Corrections, and Hydrates.

Freezing-point.			Hydrates.				
<i>m</i>	$\Delta$	$\Delta/m$	<i>a</i>	<i>L</i>	<i>L'</i>	<i>M</i>	<i>H</i>
0.45	1.52	3.35	0.839	3.42	3.30	.....	.....
0.65	2.24	3.45	0.835	3.41	3.38	.....	.....
0.85	2.91	3.43	0.832	3.41	3.34	.....	.....
0.90	3.08	3.42	0.812	3.37	3.32	.....	.....
1.05	3.58	3.41	0.818	3.38	3.40	.....	.....
1.2972	4.48	3.45	0.805	3.36	3.33	.....	.....
1.3	4.49	3.46	0.805	3.36	3.33	.....	.....
1.7	5.93	3.49	0.800	3.35	3.31	.....	.....
2.1	7.43	3.54	0.793	3.34	3.33	.....	.....
2.5945	9.29	3.58	0.782	3.32	3.32	.....	.....

Conductivity.				Weight-normal corrections.			
<i>m</i>	<i>V</i>	<i>k</i>	$\mu_s$	<i>W<sub>sol</sub></i>	<i>W<sub>salt</sub></i>	<i>W<sub>H<sub>2</sub>O</sub></i>	Correction, per cent.
0.45	2.222	0.03033	67.4	8.0042	0.26353	7.74067	1.4
0.65	1.538	0.04361	67.1	8.0735	0.38066	7.69284	2.0
0.85	1.1765	0.05680	66.8	8.1443	0.49654	7.64766	2.6
0.90	1.1111	0.05872	65.2	25.9936	1.6785	24.3151	2.7
1.05	0.9523	0.06897	65.7	8.2169	0.61492	7.60198	3.2
1.2972	0.7709	0.08395	64.7	.....	.....	.....	.....
1.3	0.7792	0.08412	64.7	26.5127	2.4245	24.0882	3.7
1.7	0.5882	0.10920	64.2	26.928	3.1705	23.7575	5.0
2.1	0.4762	0.13378	63.7	27.4457	3.9165	23.5292	5.9
2.5945	0.3854	0.16321	62.8	28.0254	4.8385	23.1869	7.3

## MIXTURE OF CALCIUM CHLORIDE AND POTASSIUM CHLORIDE.

In order that each solution should have exactly one-half the normality after mixing that it had before, the volume of the mixture was brought to exactly twice the volume by the addition of either of the constituent solutions.

TABLE 4.—Data for Mixtures of Calcium Chloride and Potassium Chloride.

Conductivity.								
$m$	$m_c$	$V_c$	$k_u$	$k$	$D$	$k_c$	$\mu_9$	$\alpha$
1.0 CaCl <sub>2</sub> .....	0.5	2.0000	0.06998	(0.04380)	0.00416	(0.04889)	84.6	0.573
0.9 KCl.....	0.45	2.2220		(0.03033)		(0.02769)	61.5	0.766
1.4 CaCl <sub>2</sub> .....	0.7	1.4285	0.09371	(0.05755)	0.00745	(0.05465)	78.1	0.529
1.3 KCl.....	0.65	1.5380		(0.04361)		(0.03906)	60.0	0.748
1.8 CaCl <sub>2</sub> .....	0.9	1.1111	0.11410	(0.07060)	0.013309	(0.06522)	72.5	0.491
1.7 KCl.....	0.85	1.1765		(0.05680)		(0.04888)	56.5	0.716
2.2 CaCl <sub>2</sub> .....	1.1	0.9090	0.13081	(0.08157)	0.01973	(0.07335)	66.7	0.452
2.1 KCl.....	1.05	0.9523		(0.06897)		(0.05746)	54.7	0.681
2.7 CaCl <sub>2</sub> .....	1.35	0.7407	0.14805	(0.09286)	0.02876	(0.08041)	59.6	0.404
2.5945 KCl.....	1.2972	0.7709		(0.08395)		(0.06765)	52.2	0.649
3.1 CaCl <sub>2</sub> .....	1.55	0.6451	0.15081	(0.09919)	0.03232	(0.05779)	55.4	0.375
2.5945 KCl.....	1.2972	0.7709		(0.08395)		(0.06502)	50.1	0.624
3.5106 CaCl <sub>2</sub> .....	1.755	0.5698	0.15239	(0.10728)	0.03879	(0.09183)	52.3	0.355
2.5945 KCl.....	1.2972	0.7709		(0.08395)		(0.06056)	46.7	0.581
Weight-normal corrections.								Freezing-point.
$m$	$W_{sol}$	$W_{salt}$	$WH_2O$	Correction, per cent.	$\Delta$			
1.0 CaCl <sub>2</sub> +0.9 KCl.....	26.7448	2.22637	24.51843	1.9	4.413			
1.4 CaCl <sub>2</sub> +1.3 KCl.....	27.3662	3.1542	22.2120	3.2	6.625			
1.8 CaCl <sub>2</sub> +1.7 KCl.....	28.0354	4.0827	23.9527	4.2	9.17			
2.2 CaCl <sub>2</sub> +2.1 KCl.....	28.6177	5.0102	23.6075	5.6	12.01			
2.7 CaCl <sub>2</sub> +2.59 KCl.....	29.4220	6.1655	23.2565	6.9	15.00			
3.1 CaCl <sub>2</sub> +2.59 KCl.....	29.8247	6.7205	23.1042	7.6	16.50			
3.51 CaCl <sub>2</sub> +2.59 KCl.....	30.2118	7.2793	22.9235	8.3	18.0			

In table 4,  $m$  is the normality of the solutions mixed. When equal volumes are mixed the resulting normality of each solution is exactly one-half of that of the solutions before mixing. This is given under  $m_c$ .  $V_c$  is the number of liters of solution that will contain a gram-molecular weight of the salt, based on  $m_c$ .  $k_u$  is the specific conductivity of the mixture. This would be the sum of the conductivities of the component solutions if no suppression of the ionization occurred. In each case the sum of these two, minus the conductivity of the mixture,  $k_u$ , gives the decrease in conductivity due to the driving back of the dissociation of the salts in question. This is given under  $D$ . This loss in conductivity is then apportioned to each electrolyte by the method already described, and the resulting conductivities are given under  $k_c$ . From this,  $\mu_s$  and  $\alpha$  are obtained.

Proceeding upon the tentative hypothesis that the calcium chloride forms the same hydrates in the presence of a salt with no hydrating power that it forms in separate solution, the values in table 5 were calculated.



TABLE 5.—*Calcium and Potassium Chlorides in the Mixture.*

Calcium chloride in the mixture.						
$m$	$m_0$	$\alpha$	$L$	$I$		
1.0 CaCl <sub>2</sub> +0.9 KCl.....	0.5	0.573	3.992	2.034		
1.4 CaCl <sub>2</sub> +1.3 KCl.....	0.7	0.529	3.829	2.769		
1.8 CaCl <sub>2</sub> +1.7 KCl.....	0.9	0.491	3.687	3.464		
2.2 CaCl <sub>2</sub> +2.1 KCl.....	1.1	0.452	3.541	4.126		
2.7 CaCl <sub>2</sub> +2.59 KCl.....	1.35	0.404	3.362	4.880		
3.1 CaCl <sub>2</sub> +2.59 KCl.....	1.55	0.375	3.256	5.462		
3.51 CaCl <sub>2</sub> +2.59 KCl.....	1.7553	0.355	3.179	6.084		
Potassium chloride in the mixture.						
$m$	$m_0$	$\alpha_1$	$\Delta$	$W_{H_2O}$	Correction, per cent.	$I_1$
1.0 CaCl <sub>2</sub> +0.9 KCl.....	0.45	0.766	1.478	753.7	24.6	1.961
1.4 CaCl <sub>2</sub> +1.3 KCl.....	0.65	0.748	2.113	655.9	34.4	3.222
1.8 CaCl <sub>2</sub> +1.7 KCl.....	0.85	0.716	2.712	608.2	39.2	4.454
2.2 CaCl <sub>2</sub> +2.1 KCl.....	1.05	0.681	3.283	538.5	46.2	6.097
2.7 CaCl <sub>2</sub> +2.59 KCl.....	1.2972	0.649	3.068	464.7	53.5	8.564
3.1 CaCl <sub>2</sub> +2.59 KCl.....	1.2972	0.624	3.021	408.0	59.2	9.605
3.51 CaCl <sub>2</sub> +2.59 KCl.....	1.2972	0.581	2.941	340.5	66.0	11.20

$\alpha$  is the dissociation of the calcium chloride in the mixture.  $L$  is the freezing-point lowering calculated from the formula  $(1.86 \times 2\alpha) + 1.86$ .  $I$  is the freezing-point lowering, corrected to 1,000 grams of solvent, which the salt would give if there were no hydration.

$\alpha_1$  is the dissociation of the potassium chloride in the mixture;  $\Delta$  is the freezing-point lowering deduced from  $[(1.86 \times \alpha) + 1.86]m_0$ ;  $W_{H_2O}$  is the weight of water acting as solvent towards the potassium chloride, deduced from  $L : L :: X : 1,000$ , which gives the amount of water taken up by the calcium chloride in the formation of hydrates when it alone is present in solution, and from the weight-normal correction for the mixture;  $I_1$  is the theoretical lowering which the potassium chloride would give if the calcium chloride formed the same hydrates in the mixture that it forms when alone in solution.

#### LOWERING DUE TO HYDRATION.

In table 6,  $\Delta_e$  is the lowering found experimentally for the mixture.  $I_e$  = sum of  $I$  and  $I_1$  in table 5.  $\text{Diff}_e = \Delta - I_e$  = lowering due to hydration.  $\Delta$  = lowering found experimentally for calcium chloride, corrected to 1,000 grams of solvent.  $I$  is the lowering the calcium chloride should have given in 1,000 grams of solvent if there were no hydration. Evidently,  $\text{Diff}_e$  and  $\text{Diff}$  should be identical if there were no change in hydration; such is not the case. Therefore, the basis assumed for the calculation of  $I$  for potassium chloride in the mixture is incorrect, as it depends upon a knowledge of the amount of water eliminated from the sphere of action as solvent by the hydration of the calcium chloride. It therefore becomes necessary to derive a formula for the calculation of the hydration of the calcium chloride in the mixture.

TABLE 6.—Comparison of Lowerings due to Hydration in Separate Solution of Calcium Chloride and in the Mixture.

$m$	$m_0$	$\Delta_c$	$I_c$	Diff <sub>c</sub>	$\Delta$	$I$	Diff.
1.0 CaCl <sub>2</sub> +0.9 KCl....	0.5	4.413	3.995	0.418	2.672	2.066	0.606
1.4 CaCl <sub>2</sub> +1.3 KCl....	0.7	6.625	5.991	0.634	4.044	2.750	1.250
1.8 CaCl <sub>2</sub> +1.7 KCl....	0.9	9.170	7.918	1.252	5.314	3.455	1.859
2.2 CaCl <sub>2</sub> +2.1 KCl....	1.1	12.01	10.223	1.782	6.896	4.100	2.799
2.7 CaCl <sub>2</sub> +2.59 KCl...	1.35	15.0	13.442	1.558	9.072	4.861	4.221
3.1 CaCl <sub>2</sub> +2.59 KCl...	15.55	16.5	15.067	1.433	11.13	5.385	5.745
3.51 CaCl <sub>2</sub> +2.59 KCl..	1.7553	18.0	17.284	0.712	14.10	5.970	8.130

The following formulæ are for calculating lowering due to hydration, in a binary mixture of electrolytes, where one salt has no hydrating power:

$X$  = lowering in degrees due to hydration of the salt with hydrating power in the mixture.

$I$  = theoretical lowering which the salt with hydrating power should give in the mixture in question, at the corrected dissociation, if there were no hydration.

$v$  = number of liters that contain a gram-molecule of the salt with hydrating power, at the normality it has in the mixture.

Then,

$$(X+I)v = \Delta/m$$

$s$  = correction to 1,000 grams of solvent, necessary in the mixture.

$$(X+I)v - (X+I)vs = L'$$

$X'$  = amount of water acting as solvent towards the salt with no hydrating power.

$$L : L' :: X' : 1000$$

$L = (1.86 \times 2a) + 1.86$ , in a ternary electrolyte, where  $a$  represents the corrected dissociation of the salt with hydrating power in the mixture.

$$\frac{(1.86 \times 2a) + 1.86}{(X+I)v - (X+I)vs} 1000 = X'$$

But taking into account the weight-normal correction also, in the mixture in question, the above becomes

$$\left[ \frac{(1.86 \times 2a) + 1.86}{(X+I)v - (X+I)vs} 1000 \right] - 10S = \begin{cases} \text{amount of water actually acting as solvent} \\ \text{towards the salt with no hydrating power.} \end{cases}$$

Putting this into the form of a percentage correction,

$$\frac{(1.86 \times 2a) + 1.86}{(X+I)v - (X+I)vs} - \frac{S}{10} = \begin{cases} \text{the per cent by which } I \text{ for the salt with little} \\ \text{or no hydrating power must be divided.} \end{cases}$$

$a'$  = corrected dissociation in mixture of the salt with no hydrating power,

$[(1.86 \times a') + 1.86]m$  = lowering it would give in 1,000 grams of solvent if it is a binary electrolyte.

$m$  = normality of the salt with no hydrating power.

Then,

$$\frac{1.86m(a'+1)}{\frac{1.86(2a+1)}{(X+I)(v-vs)} - \frac{S}{100}} + X + I = \begin{cases} \text{lowering found experimentally for} \\ \text{the mixture.} \end{cases}$$

By means of the preceding formula the value of  $X$  has been calculated for various concentrations used in the mixture of calcium chloride and potassium chloride, and the results are given in table 7. The significance of the symbols has already been given.

#### CALCIUM CHLORIDE.

TABLE 7.—Hydration of Calcium Chloride in the Mixture.

$m$	$M_c$	$a$	$L$	$I$	$X$	$\Delta/m$	$L'$	$M$	$H$
1.0 $\text{CaCl}_2 + 0.9 \text{ KCl}$ ....	0.5	0.573	3.920	2.034	0.456	4.981	4.886	10.2	23.8
1.4 $\text{CaCl}_2 + 1.3 \text{ KCl}$ ....	0.7	0.529	3.829	2.769	0.909	5.254	5.086	13.7	19.6
1.8 $\text{CaCl}_2 + 1.7 \text{ KCl}$ ....	0.9	0.491	3.687	3.464	1.537	5.556	5.323	17.1	19.0
2.2 $\text{CaCl}_2 + 2.1 \text{ KCl}$ ....	1.1	0.452	3.541	4.126	2.291	5.834	5.507	19.8	18.0
2.7 $\text{CaCl}_2 + 2.59 \text{ KCl}$ ....	1.35	0.404	3.362	4.880	2.940	5.978	5.387	20.9	15.5
3.1 $\text{CaCl}_2 + 2.59 \text{ KCl}$ ....	1.55	0.375	3.256	5.462	3.601	5.847	5.403	22.1	14.3
3.51 $\text{CaCl}_2 + 2.59 \text{ KCl}$ ...	1.7553	0.355	3.179	6.064	4.320	5.928	5.436	23.1	13.1

In order to compare the hydrates formed by calcium chloride in separate solution with those which it forms in the mixture with potassium chloride, the values of  $M$  are plotted against the concentrations as abscissas in fig. 1.

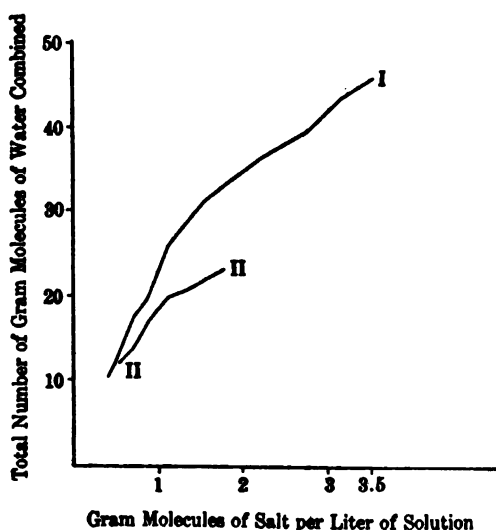


FIG. 1.

I. Calcium Chloride Alone.

II. Calcium Chloride Mixed with Potassium Chloride.

of the calcium chloride or the resulting ions combine depends upon the number of molecules of water present to one molecule of the calcium chloride. If, now, instead of increasing the number of grams of salt with hydrating power present in a given solution, and thus diminishing the amount of water, we add to the calcium chloride a substance like potassium chloride and then make up to the former volume, it is evident that, there being less water present, the amount of water with which each

It is seen that while the value of  $M$  increases with increase in concentration, in general, in the mixture as in separate solution,  $M$  is less in the mixture than in separate solution of calcium chloride. This is just what we should expect, since there is less water present as solvent in the mixture of calcium chloride and potassium chloride, at any given concentration of the calcium chloride, than there is at the same concentration of the single solution of calcium chloride. It is evident, from previous work, that while the total number of gram-molecules of water combined increases, in general, with increase in concentration, the molecular hydration decreases with increase in concentration. That is, the amount of water with which a molecule

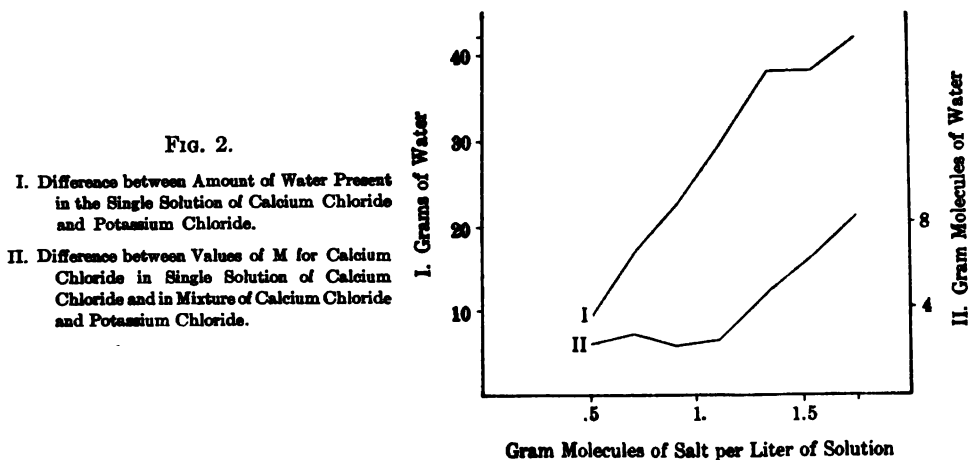
molecule or ion of calcium chloride will combine will be diminished; that is, the value of  $M$  will be diminished.

In order to compare the difference between the amount of water present acting as solvent towards the calcium chloride in the single solution and in the mixture, with the difference in the values of  $M$  in the two cases, we give in table 8, under  $D_{H_2O}$ , the difference between the number of grams of water present as solvent in the separate solution of calcium chloride and in the mixture at the respective concentrations; under  $D_m$ , the difference in the values of  $M$  for the separate solution of the calcium chloride and in the mixture at the same concentrations.

TABLE 8.

$m$	$D_{H_2O}$	$D_m$
0.5	9	2.4
0.7	17	2.8
0.9	22	2.34
1.1	29	2.61
1.35	38	4.99
1.55	38	6.62
1.7553	42	8.36

These results are plotted in curves as fig. 2. For the first four concentrations the values of  $M$  decrease by the same amount, since the amount of potassium chloride added is increased as the calcium chloride is increased. Consequently



the curve for the difference in the values of  $M$  is approximately parallel to the axis of abscissa (concentration). Referring to table 7, it will be seen that the difference between successive values of  $M$  diminishes with increase in concentration, until finally, in the mixture containing 2.7 N calcium chloride and 2.59 N potassium chloride,  $M$  has the value 20.9. The effect of the potassium chloride on the amount of water with which the calcium chloride can combine is such that, although the

same amount of potassium chloride is added to the succeeding mixtures, the calcium chloride can increase its water of hydration only slightly, and by a constant difference, with increase in the concentration of the calcium chloride added. Consequently, there is increasing deviation, in fig. 1, between the curve representing the value of  $M$  for the single solution and that representing  $M$  for the mixture. In fig. 2 the difference between the values of  $M$  for calcium chloride in the separate solution and in the mixture is approximately proportional to the difference in the amount of water present acting as solvent towards the calcium chloride in the separate solution and in the mixture. This is shown by curve II.

It must be borne in mind that these results are based on the assumption that calcium chloride breaks down at once into  $\text{Ca}^{++}$ ,  $\text{Cl}^-$ ,  $\text{Cl}^-$ ; also, that the entire decrease in conductivity upon mixing is due to re-formation of the molecules, whereas a part of the decrease is certainly due to viscosity and friction of the ionic spheres, as already mentioned.

*In order to ascertain the effect upon the hydrates formed, a pair of salts, both of which have hydrating power, was next studied.*

For this purpose it was considered desirable to investigate, first, a case where both the salts employed have a large hydrating power, and where the hydrating power of the two salts in single solution is of the same order of magnitude. Calcium chloride and magnesium chloride fulfill these conditions. (Tables 9 to 11.)

TABLE 9.—Calcium Chloride—Data for Freezing-point and Conductivity Measurements, Weight-normal Corrections, and Hydrates.

$m$	Freezing-point.		Hydrates.				
	$\Delta$	$\Delta/m$	$a$	$L$	$L'$	$M$	$H$
0.15	0.74	4.93	0.677	4.38	4.91	6.0	40.2
0.25	1.265	5.06	0.653	4.29	5.03	8.2	32.8
0.35	1.801	5.15	0.633	4.22	5.11	9.7	27.8
0.45	2.35	5.22	0.598	4.08	5.17	11.7	25.9
0.65	3.55	5.62	0.565	3.96	5.53	15.7	24.3
0.85	5.05	5.94	0.534	3.85	5.83	18.9	22.3
1.05	6.65	6.33	0.505	3.74	6.18	21.9	20.9
1.25	8.41	6.73	0.482	3.65	6.50	24.3	19.5
1.45	10.51	7.25	0.455	3.55	6.99	27.3	18.8

$m$	Conductivity.			Weight-normal corrections.			
	$V$	$k$	$\mu_0$	$W_{\text{sol}}$	$W_{\text{salt}}$	$WH_2O$	Correction, per cent.
0.15	6.6666	0.01499	99.9	25.3227	0.41625	24.90645	0.4
0.25	4.0000	0.02407	96.3	25.5423	0.69375	24.84855	0.6
0.35	2.8571	0.03270	93.4	25.8040	0.97125	24.83275	0.7
0.45	2.2222	0.03969	88.2	26.0110	1.24875	24.76225	1.0
0.64	1.5380	0.05424	83.4	26.4384	1.80375	24.63465	1.5
0.83	1.1765	0.06690	78.7	26.8816	2.35875	24.52285	1.9
1.05	0.9523	0.07824	74.5	27.2846	2.91375	24.37085	2.5
1.25	0.8000	0.08885	71.1	27.6792	3.46875	24.21045	3.2
1.45	0.6897	0.09738	67.2	28.1293	4.02375	24.10555	3.6

## MAGNESIUM CHLORIDE.

TABLE 10.—*Magnesium Chloride—Data for Freezing-point and Conductivity Measurements, Weight-normal Corrections, and Hydrates.*

<i>m</i>	Freezing-point.		Hydrates.				
	$\Delta$	$\Delta/m$	$\alpha$	<i>L</i>	<i>L'</i>	<i>M</i>	<i>H</i>
0.15	0.747	4.98	0.705	4.48	4.97	5.5	36.5
0.25	1.306	5.22	0.667	4.34	5.20	9.2	36.7
0.35	1.910	5.46	0.625	4.19	5.43	12.7	36.3
0.45	2.537	5.64	0.601	4.10	5.58	14.9	33.1
0.65	3.854	5.93	0.570	3.98	5.86	17.8	27.4
0.85	5.404	6.36	0.525	3.81	6.26	21.7	25.6
1.05	7.191	6.84	0.489	3.68	6.70	25.1	23.9
1.25	9.236	7.39	0.456	3.56	7.20	28.1	22.5
1.45	11.470	7.91	0.417	3.41	7.67	30.9	21.3

<i>m</i>	Conductivity.			Weight-normal corrections.			
	<i>V</i>	<i>k</i>	$\mu_0$	<i>W<sub>sat</sub></i>	<i>W<sub>sat</sub></i>	<i>W<sub>H<sub>2</sub>O</sub></i>	Correction, per cent.
0.15	6.6666	0.01364	90.9	25.2954	0.3572	24.9382	0.2
0.25	4.0000	0.02153	86.1	25.5072	0.5954	24.9118	0.4
0.35	2.8571	0.02824	80.7	25.7066	0.8333	24.8731	0.5
0.45	2.2222	0.03618	80.4	25.8825	1.1710	24.8108	0.8
0.65	1.5380	0.04786	73.6	26.2378	1.5490	24.6898	1.2
0.85	1.1765	0.05761	67.8	26.6460	2.0243	24.6217	1.5
1.05	0.9523	0.06628	63.1	26.0011	2.5006	24.5005	2.0
1.25	0.8000	0.07350	58.8	27.3538	2.9768	24.3770	2.5
1.45	0.6896	0.07804	53.8	27.7095	3.4532	24.2563	3.0

## MIXTURE OF CALCIUM CHLORIDE AND MAGNESIUM CHLORIDE.

TABLE 11.—*Data for Mixtures of Calcium Chloride and Magnesium Chloride.*

Conductivity.								
<i>m</i>	<i>m<sub>c</sub></i>	<i>V<sub>c</sub></i>	<i>k<sub>u</sub></i>	<i>k</i>	<i>D</i>	<i>k<sub>c</sub></i>	$\mu_0$	$\alpha$
0.3 CaCl <sub>2</sub> .....	0.15	6.6666	0.026923	(0.01499)	0.00171	(0.01406)	93.8	0.636
0.3 MgCl <sub>2</sub> .....	0.15	6.6666		(0.01364)		(0.01286)	85.7	0.664
0.5 CaCl <sub>2</sub> .....	0.25	4.0000	0.041214	(0.02407)	0.00439	(0.02171)	86.8	0.605
0.5 MgCl <sub>2</sub> .....	0.25	4.0000		(0.02153)		(0.01950)	78.0	0.605
0.7 CaCl <sub>2</sub> .....	0.35	2.8571	0.053615	(0.03270)	0.00732	(0.02882)	82.3	0.558
0.7 MgCl <sub>2</sub> .....	0.35	2.8571		(0.02824)		(0.02480)	70.9	0.549
0.9 CaCl <sub>2</sub> .....	0.45	2.2222	0.065080	(0.03969)	0.01079	(0.03382)	75.2	0.510
0.9 MgCl <sub>2</sub> .....	0.45	2.2222		(0.03618)		(0.03126)	69.5	0.538
1.3 CaCl <sub>2</sub> .....	0.65	1.5380	0.082101	(0.05424)	0.02000	(0.04326)	66.9	0.454
1.3 MgCl <sub>2</sub> .....	0.65	1.5380		(0.04786)		(0.03857)	59.3	0.460
1.7 CaCl <sub>2</sub> .....	0.85	1.1765	0.094339	(0.06690)	0.03017	(0.05093)	59.9	0.406
1.7 MgCl <sub>2</sub> .....	0.85	1.1765		(0.05761)		(0.04341)	51.1	0.396
2.1 CaCl <sub>2</sub> .....	1.05	0.9523	0.10078	(0.07824)	0.04374	(0.05526)	52.6	0.357
2.1 MgCl <sub>2</sub> .....	1.05	0.9523		(0.06628)		(0.04552)	43.4	0.336
2.5 CaCl <sub>2</sub> .....	1.25	0.8000	0.10278	(0.08885)	0.05957	(0.05791)	46.3	0.314
2.5 MgCl <sub>2</sub> .....	1.25	0.8000		(0.07350)		(0.04487)	35.9	0.278
2.9 CaCl <sub>2</sub> .....	1.45	0.6896	0.10007	(0.09738)	0.07536	(0.05884)	40.6	0.275
2.9 MgCl <sub>2</sub> .....	1.45	0.6896		(0.07804)		(0.04122)	28.4	0.220

TABLE 11—Continued.

Weight-normal corrections.					Fr.-pt.
<i>m</i>	<i>W<sub>sol</sub></i>	<i>W<sub>salt</sub></i>	<i>W<sub>H<sub>2</sub>O</sub></i>	Correction, per cent.	$\Delta$
0.3 CaCl <sub>2</sub> +0.3 MgCl <sub>2</sub> .....	25.6460	0.77345	24.87255	0.5	1.553
0.5 CaCl <sub>2</sub> +0.5 MgCl <sub>2</sub> .....	26.0314	1.28915	24.74225	1.0	2.704
0.7 CaCl <sub>2</sub> +0.7 MgCl <sub>2</sub> .....	26.4594	1.80475	24.65465	1.4	4.053
0.9 CaCl <sub>2</sub> +0.9 MgCl <sub>2</sub> .....	26.8453	2.32045	24.52485	1.9	5.543
1.3 CaCl <sub>2</sub> +1.3 MgCl <sub>2</sub> .....	27.6088	3.35175	24.25705	3.0	9.320
1.7 CaCl <sub>2</sub> +1.7 MgCl <sub>2</sub> .....	28.3821	4.38305	23.99905	4.0	13.50
2.1 CaCl <sub>2</sub> +2.1 MgCl <sub>2</sub> .....	29.1096	5.41435	23.69525	5.2	19.50
2.5 CaCl <sub>2</sub> +2.5 MgCl <sub>2</sub> .....	29.8333	6.44555	23.38775	6.5	27.25
2.9 CaCl <sub>2</sub> +2.9 MgCl <sub>2</sub> .....	30.5280	7.47695	23.05105	8.8	37.0

In table 12,  $m_e$ =normal concentration of each salt in the mixture.  $\alpha$ =dissociation of each salt in the mixture, as given in table 11.  $mL$ =lowering of freezing point, calculated from formula  $[(1.86 \times 2\alpha) + 1.86]m$ . The correction percentage is deduced on the assumption that the two salts form the same hydrates in the mixture that they form in separate solutions. Upon this assumption the amount of water which each salt would eliminate from the sphere of action as solvent is calculated from the formula

$$1000 - \left[ \frac{L}{L_1} \times 1000 \right]$$

The values for magnesium chloride and calcium chloride are added together, and to this is added also the difference between 1,000 grams and the amount of water actually present in one liter as given by the weight-normal corrections. This, then, is given as a percentage correction in the column headed "Correction, per cent." The value  $mL$  is divided by this percentage and the result given under  $\Delta$ .

Evidently the sum of the values of  $\Delta$  for calcium chloride and magnesium chloride, as thus found, should equal the lowering found experimentally for the mixture in question. These values are placed side by side, for comparison, in table 12.

TABLE 12.—Conditions in the Mixture of Calcium Chloride and Magnesium Chloride.

<i>m</i>	<i>m<sub>e</sub></i>	$\alpha$	<i>mL</i>	Correction, per cent.	$\Delta$	$\Delta$ (calculated)	$\Delta$ (exp.)	Diff.
0.3 CaCl <sub>2</sub> } 0.3 MgCl <sub>2</sub> } ..	0.15	{0.636 0.664	{0.634 0.660	78.9	{0.803 0.823	1.626	1.553	0.073
0.5 CaCl <sub>2</sub> } 0.5 MgCl <sub>2</sub> } ..		{0.589 0.605	{1.012 1.027		{1.488 1.510			
0.7 CaCl <sub>2</sub> } 0.7 MgCl <sub>2</sub> } ..	0.25	{0.558 0.549	{1.378 1.366	68.0	{2.345 2.325	2.998	2.704	0.294
0.9 CaCl <sub>2</sub> } 0.9 MgCl <sub>2</sub> } ..		{0.510 0.538	{1.690 1.738		{3.298 3.392			
1.3 CaCl <sub>2</sub> } 1.3 MgCl <sub>2</sub> } ..	0.35	{0.454 0.460	{2.380 2.321	58.8	{5.998 6.035	4.670	4.053	0.617
1.7 CaCl <sub>2</sub> } 1.7 MgCl <sub>2</sub> } ..		{0.408 0.396	{2.865 2.832		{1.13 11.00			
2.1 CaCl <sub>2</sub> } 2.1 MgCl <sub>2</sub> } ..	0.45	{0.357 0.336	{3.346 3.264	51.2	{22.85 22.29	6.690	5.543	1.147
	0.65			38.5		12.033	9.320	2.713
	0.85			25.8		22.13	13.5	8.629
	1.05			14.7		45.14	19.5	25.64

It is unnecessary to extend these calculations to the remaining, more concentrated mixtures, since it is evident that the differences between the values calculated on the basis that the two salts form the same hydrates in separate solutions that they form in the mixtures, and the values for  $\Delta$  obtained experimentally become increasingly larger with increase in concentration. It is further evident that the hypothesis is untenable from the fact that it would call for the elimination of 944 grams of water per liter of solution in the case of the 2.5 N mixture of the above salts, and of 1,047 grams in the case of the 2.9 N mixture.

At the moment of mixing the two solutions, each salt is prevented from forming the hydrate which it ordinarily forms in separate solution by the amount of water which has been eliminated from the sphere of action as solvent in the formation of the hydrate of the other component of the mixture. Consequently, for the more dilute solutions at least, the hydrates formed by a salt in separate solution should be related to the hydrates formed by the same salt in the mixture at corresponding concentrations, as the amount of water present as solvent in the single solution is related to the amount present as solvent in the mixture. For example, take calcium chloride and magnesium chloride, 0.15 N solutions of each. Referring to tables 9 and 10, if  $X$  represents the unknown value of  $M$  for calcium chloride, in the mixture  $6 : X :: 1,000 : 897$ . 6.0 is the value of  $M$  for 0.15 N calcium chloride in separate solution, and this has been corrected to 1,000 grams of solvent. The figure 897 is found by subtracting from 1,000 the number of grams of water with which the magnesium chloride combines when it forms the hydrate indicated for the concentration in question in table 10, plus the difference between the amount of water present in the solution and 1,000 grams, as given by the weight-normal correction.

Having thus obtained the values of  $M$  for the salts in the mixture, it is possible to solve for  $L'$  from the equation

$$M = \frac{1000 - \left[ \frac{L}{L'} \times 1000 \right]}{18}$$

where  $L$  represents the theoretical lowering found for the salt by calculating it from the value of  $\alpha$ , which has been determined for the mixture in question. This value of  $L'$  must then be corrected, in order to obtain the value as it would be observed, by dividing it by the proper per cent. This percentage correction is found by deducing the number of grams of water eliminated as water of hydration by the other salt in the mixture, basing the calculation upon the value of  $M$  worked out for the mixture. To this must be added the percentage correction which the weight-normal correction has given.

The sum of these values for  $L'$  for the two salts in the mixture should then be equal to  $\Delta$  as found experimentally for the mixture, provided this hypothesis is correct. In table 13 the values thus obtained are given.

$M_e$  = the value for  $M$  deduced from the proportion.

$L'_e$  = the value for  $L'$ , with proper percentage correction.

Sum = sum of the two values for  $L'_e$  for the two salts multiplied by the normality of the solution.

$\Delta$  = the lowering found experimentally for the same mixture.



The other symbols employed have the usual significance.

Without further extending this method of calculation, it is evident that it does not give the true value of the hydrates formed, and that the hydrating power is larger for the more concentrated mixtures than would be indicated by the proportions given below.

This is just what we should expect, since with increasing hydration we do not have the process of loss of water from the hydrates formed in separate solution going on to the end in the mixture, but instead we have, necessarily, a condition of equilibrium between the hydrating powers of the two salts. Also, as a direct result, the amount of water thus left uncombined affects the final composition of the hydrates, as already indicated.

This condition of equilibrium is not represented by the proportions given above, since the amount of water playing the part of solvent is not that indicated by these proportions.

TABLE 13.—*Freezing-point Lowering, Calculated and Found.*

<i>m</i>	<i>m<sub>s</sub></i>	<i>M</i>	<i>M<sub>c</sub></i>	<i>L</i>	<i>L'</i>	<i>L<sub>c</sub><sup>cor.</sup></i>	Sum.	Δ
0.3 CaCl <sub>2</sub> .....	0.15	6.0	5.4	4.224	4.682	5.16	1.57	1.553
0.3 MgCl <sub>2</sub> .....	0.15	5.5	4.9	4.330	4.748	5.29		
0.5 CaCl <sub>2</sub> .....	0.25	8.2	6.8	4.109	4.685	5.52	2.74	2.704
0.5 MgCl <sub>2</sub> .....	0.25	9.2	7.8	4.050	4.715	5.44		
0.7 CaCl <sub>2</sub> .....	0.35	9.7	7.5	3.936	4.547	5.71	3.97	4.053
0.7 MgCl <sub>2</sub> .....	0.35	12.7	10.5	3.902	4.808	5.64		
0.9 CaCl <sub>2</sub> .....	0.45	11.7	8.6	3.755	4.438	5.77	5.26	5.543
0.9 MgCl <sub>2</sub> .....	0.45	14.9	11.8	3.862	4.897	5.92		
1.3 CaCl <sub>2</sub> .....	0.65	15.7	10.7	3.548	4.394	5.94	7.74	9.32
1.3 MgCl <sub>2</sub> .....	0.65	17.8	12.8	3.570	4.639	5.97		
1.7 CaCl <sub>2</sub> .....	0.85	18.9	11.5	3.371	4.251	6.06	10.21	13.5
1.7 MgCl <sub>2</sub> .....	0.85	21.7	14.3	3.332	4.487	5.96		

If we consider that the values of *M* for calcium chloride and for magnesium chloride in separate solutions, since their hydrating powers are nearly equal, represent the relative hydrating powers under the same conditions for the two salts, at the concentration corresponding to any pair of values of *M*, then it becomes possible to calculate the approximate composition of the hydrates of calcium chloride and magnesium chloride in the mixture. Selecting, for example, the mixture consisting of 1 part of 1.7 N calcium chloride and 1 part of 1.7 N magnesium chloride, then:

Let *X* equal the number of grams of water eliminated in the formation of the hydrate of calcium chloride which occurs in the mixture in question. If the hydrates of calcium chloride and magnesium chloride in the mixture are related as they are in separate solutions, they will be to each other as 18.9:21.7 (see tables 9 and 10), hence,  $\frac{217}{189}X$  = the number of grams of water eliminated in the formation of hydrate of magnesium chloride in the mixture.

From the equation

$$M = \frac{1000 - \left[ \frac{L}{L'} \times 1000 \right]}{18}$$

we have

$$X = 1000 - \frac{3371}{L'_{Ca}} \quad (1)$$

where 3.371 is the lowering found for 0.85 N calcium chloride by calculation from the value of  $a$  given in table 11, and  $L'_{Ca}$  = the lowering observed for calcium chloride, corrected properly for water less than 1,000 grams, and multiplied by  $m$ .

Similarly,

$$\frac{217}{189} X = 1000 - \frac{3332}{L'_{Mg}} \quad (2)$$

Let  $L'_0$  = *observed* lowering due to magnesium chloride. Then,  $13.5^\circ - L'_0$  = *observed* lowering due to calcium chloride (*vide* table 11).

Then,

$$L'_0 = \frac{L'_{Mg} \times 0.85}{1 - \frac{X}{1000} - \frac{4}{100}} \quad (3)$$

where 0.85 is the normality in question, and the denominator is the necessary percentage correction, based upon the value of  $X$  and the correction given in table 11.

Similarly,

$$13.5 - L'_0 = \frac{L'_{Ca} \times 0.85}{1 - \frac{217}{189} X - \frac{4}{1000}} \quad (4)$$

From equation (1),

$$L'_{Ca} = \frac{3371}{1000 - X} \quad (5)$$

From equation (2),

$$L'_{Mg} = \frac{3332}{1.000 - 1.148X} \quad (6)$$

Eliminating  $L'_0$  by combining equations (3) and (4), and then substituting the values of  $L'_{Ca}$  and  $L'_{Mg}$  from (5) and (6), it becomes possible to solve for  $X$ . By this method the values of  $M$  for calcium chloride and magnesium chloride in this mixture are found to be 17.1 and 19.6, respectively.

By the above methods the values of  $M$  for the mixtures between 0.9 N and 2.9 N have been derived, and are given in table 14, under  $M_c$ . The abbreviations at the top of each column have the usual significance, the suffix  $c$  indicating that the values are for the salt *in the mixture*.

For the sake of comparison, the values of  $M$  for calcium chloride and magnesium chloride in separate solutions are plotted as curves against concentration (as axis of abscissas). Upon the same sheet are drawn similar curves for the values of  $M$  in the mixture.

TABLE 14.—Hydration in the Mixture of Calcium Chloride and Magnesium Chloride.

$m$	$m_c$	$a$	$L_c$	$M$	$\Delta$	Sp. gr. cor.	$M_c$	$H_c$
1.3 CaCl <sub>2</sub> .....	0.65	0.454	3.548	15.74	9.32	3.0	14.5	22.3
1.3 MgCl <sub>2</sub> .....	0.65	0.460	3.570	17.79			16.4	25.2
1.7 CaCl <sub>2</sub> .....	0.85	0.406	3.371	18.92			17.1	20.1
1.7 MgCl <sub>2</sub> .....	0.85	0.396	3.332	21.73	13.5	4.0	19.6	23.1
2.1 CaCl <sub>2</sub> .....	1.05	0.357	3.187	21.92			19.8	18.9
2.1 MgCl <sub>2</sub> .....	1.05	0.336	3.264	25.06			22.7	21.6
2.5 CaCl <sub>2</sub> .....	1.25	0.314	3.028	24.32	27.25	5.2	22.8	18.2
2.5 MgCl <sub>2</sub> .....	1.25	0.278	2.895	28.14			26.3	21.0
2.9 CaCl <sub>2</sub> .....	1.45	0.275	2.883	27.29			25.9	17.9
2.9 MgCl <sub>2</sub> .....	1.45	0.220	2.479	30.86	37.0	7.8	28.9	19.9

Upon comparing curve I, fig. 3, the hydration of magnesium chloride alone, with curve IV, the hydration of the calcium chloride in the mixture, it will be seen that where I rises IV falls, and *vice versa*. This is exactly what we should expect, since an increase in the hydrating power of magnesium chloride should result in a corresponding decrease in the amount of water with which the calcium chloride would be able to combine in the mixture, unless a corresponding increase in the hydrating power of the calcium chloride in separate solution should also occur. Again, comparing curves I and II, and III and IV, the hydrates in separate solution and in the mixture are of the same general order of magnitude, except where the presence of the one salt in the mixture alters the composition of the hydrate formed by the other.

*It was thought desirable to compare the effect of a salt with less hydrating power mixed with one of greater hydrating power.*

For this purpose calcium chloride and strontium chloride were selected, the hydrating power of strontium chloride being somewhat less than that of calcium chloride.

The data for the separate solutions of calcium chloride have already been given. Those of strontium chloride follow in tables 15 and 16.

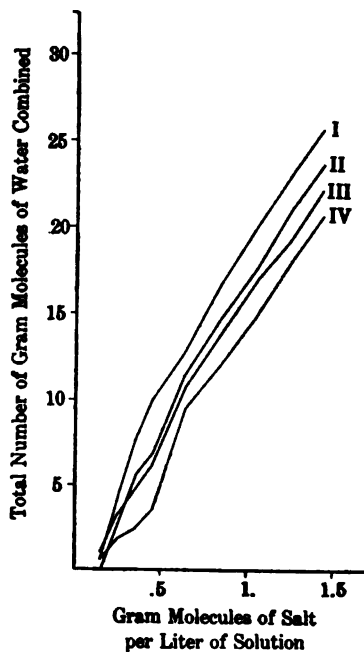


FIG. 3.

- I. Magnesium Chloride Alone.
- II. Magnesium Chloride Mixed with Calcium Chloride.
- III. Calcium Chloride Alone.
- IV. Calcium Chloride Mixed with Magnesium Chloride.

## STRONTIUM CHLORIDE.

TABLE 15.—*Strontium Chloride—Data for Freezing-point and Conductivity Measurements, Weight-normal Corrections, and Hydrates.*

Freezing-point.			Hydrates.				
<i>m</i>	$\Delta$	$\Delta/m$	<i>a</i>	<i>L</i>	<i>L</i>	<i>M</i>	<i>H</i>
0.15	0.753	5.02	0.747	4.64	4.99	3.9	26.0
0.25	1.249	5.00	0.705	4.48	4.97	5.5	22.0
0.35	1.774	5.07	0.678	4.39	5.03	7.1	20.3
0.45	2.333	5.18	0.655	4.30	5.13	9.0	20.0
0.65	3.521	5.42	0.616	4.15	5.34	12.4	19.1
0.85	4.863	5.72	0.581	4.02	5.60	15.7	18.5
1.05	6.354	6.05	0.553	3.93	5.91	18.7	17.8
1.2354	7.861	6.36	0.522	3.80	6.17	21.3	17.2

Conductivity.				Weight-normal corrections.			
<i>m</i>	<i>V</i>	<i>k</i>	$\mu_0$	<i>W<sub>sol</sub></i>	<i>S<sub>salt</sub></i>	<i>WH<sub>2</sub>O</i>	Correction, per cent.
0.15	6.6666	0.01538	102.5	25.5325	0.59437	24.94810	0.3
0.25	4.0000	0.02418	96.7	25.8496	0.99060	24.85898	0.6
0.35	2.8571	0.03259	93.1	26.1900	1.38688	24.8031	0.8
0.45	2.2222	0.04048	90.0	26.5388	1.7831	24.7557	1.0
0.65	1.5380	0.05502	84.6	27.1944	2.5756	24.6188	1.5
0.85	1.1764	0.06782	79.8	27.8553	3.3681	24.4872	2.1
1.05	0.9523	0.07980	76.0	28.5672	4.1606	24.4066	2.4
1.2354	0.8945	0.08861	71.7	29.1297	4.8954	24.2344	3.1

TABLE 16.—*Mixture of Calcium Chloride and Strontium Chloride—Data for Conductivity Measurements and Weight-normal Corrections.*

Conductivity.								
<i>m</i>	<i>m<sub>c</sub></i>	<i>V<sub>c</sub></i>	<i>k<sub>c</sub></i>	<i>k</i>	<i>D</i>	<i>k<sub>0</sub></i>	$\mu_0$	<i>a</i>
0.3 CaCl <sub>2</sub> .....	0.15	6.6666	0.01499	0.02824	0.00213	0.13840	92.3	0.625
0.3 SrCl <sub>2</sub> .....	0.15	6.6666	0.01538			0.01440	96.0	0.699
0.5 CaCl <sub>2</sub> .....	0.25	4.0000	0.02407	0.04398	0.00428	0.02177	87.1	0.590
0.5 SrCl <sub>2</sub> .....	0.25	4.0000	0.02418			0.02220	83.8	0.647
0.7 CaCl <sub>2</sub> .....	0.35	2.8571	0.03270	0.05188	0.00710	0.02890	82.6	0.560
0.7 SrCl <sub>2</sub> .....	0.35	2.8571	0.03259			0.02929	83.7	0.610
0.9 CaCl <sub>2</sub> .....	0.45	2.2222	0.03969	0.07049	0.00968	0.03446	76.6	0.519
0.9 SrCl <sub>2</sub> .....	0.45	2.2222	0.04048			0.03603	80.1	0.583
1.3 CaCl <sub>2</sub> .....	0.65	1.5380	0.05424	0.09073	0.01852	0.04424	68.1	0.461
1.3 SrCl <sub>2</sub> .....	0.65	1.5380	0.05502			0.04649	71.5	0.521
1.7 CaCl <sub>2</sub> .....	0.85	1.1765	0.06690	0.10556	0.02918	0.05117	60.2	0.408
1.7 SrCl <sub>2</sub> .....	0.85	1.1765	0.06782			0.05439	64.0	0.466
2.1 CaCl <sub>2</sub> .....	1.05	0.9523	0.07824	0.11428	0.04376	0.05458	52.0	0.352
2.1 SrCl <sub>2</sub> .....	1.05	0.9523	0.07980			0.05970	56.9	0.414

Weight-normal corrections.					Fr.-pt.
<i>m</i>	<i>W<sub>sol</sub></i>	<i>W<sub>salt</sub></i>	<i>WH<sub>2</sub>O</i>	Correction, per cent.	$\Delta$
0.3 CaCl <sub>2</sub> +0.3 SrCl <sub>2</sub> .....	25.8463	1.0106	24.8357	0.7	1.503
0.5 CaCl <sub>2</sub> +0.5 SrCl <sub>2</sub> .....	26.4106	1.6844	24.7262	1.1	2.626
0.7 CaCl <sub>2</sub> +0.7 SrCl <sub>2</sub> .....	26.9452	2.3581	24.5871	1.7	3.906
0.9 CaCl <sub>2</sub> +0.9 SrCl <sub>2</sub> .....	27.4711	3.0319	24.4392	2.2	5.310
1.3 CaCl <sub>2</sub> +1.3 SrCl <sub>2</sub> .....	28.5671	4.3794	24.1877	3.3	8.682
1.7 CaCl <sub>2</sub> +1.7 SrCl <sub>2</sub> .....	29.6381	5.7269	23.9112	4.4	12.924
2.1 CaCl <sub>2</sub> +2.1 SrCl <sub>2</sub> .....	30.6744	7.0744	23.6081	5.6	18.290

## MIXTURE OF CALCIUM CHLORIDE AND STRONTIUM CHLORIDE.

For the sake of comparison, the lowerings of the freezing-point which would be obtained from the mixture of calcium chloride and strontium chloride are given in table 17, basing them upon the same method of calculation as that already given in detail for table 13. The symbols used have the same significance in the two tables.

TABLE 17.—Freezing-point Lowering, Calculated and Found—Mixture of Calcium Chloride and Strontium Chloride.

$m$	$m_c$	$M$	$M_c$	$L$	$L'_c$	$L_c^{cor.}$	Sum.	$\Delta$
0.3 CaCl <sub>2</sub> .....	0.15	6.0	5.6	4.186	4.65	5.00	1.548	1.503
0.3 SrCl <sub>2</sub> .....	0.15	3.9	3.5	4.461	4.76	5.32		
0.5 CaCl <sub>2</sub> .....	0.25	8.2	7.3	4.056	4.67	5.16	2.646	2.626
0.5 SrCl <sub>2</sub> .....	0.25	5.5	4.6	4.266	4.65	5.43		
0.7 CaCl <sub>2</sub> .....	0.35	9.7	8.3	3.942	4.63	5.26	3.771	3.906
0.7 SrCl <sub>2</sub> .....	0.35	7.1	5.7	4.127	4.60	5.51		
0.9 CaCl <sub>2</sub> .....	0.45	11.7	9.5	3.791	4.57	5.36	4.979	5.370
0.9 SrCl <sub>2</sub> .....	0.45	9.0	6.9	4.030	4.60	5.70		
1.3 CaCl <sub>2</sub> .....	0.65	15.7	11.7	3.576	4.53	5.56	7.465	8.682
1.3 SrCl <sub>2</sub> .....	0.65	12.4	8.5	3.797	4.48	5.92		
1.7 CaCl <sub>2</sub> .....	0.85	18.9	12.8	3.378	4.39	5.61	9.877	12.924
1.7 SrCl <sub>2</sub> .....	0.85	15.7	9.7	3.593	4.35	6.00		
2.1 CaCl <sub>2</sub> .....	1.05	21.9	13.3	3.171	4.17	5.49	11.990	18.290
2.1 SrCl <sub>2</sub> .....	1.05	18.7	10.3	3.400	4.17	5.92		

It will be noted that in table 17, again, as in the case of the mixture of calcium chloride and magnesium chloride, the difference between the lowering as calculated upon the hypothesis that, for the more dilute solutions, at least, the hydrates formed by a salt in separate solution are related to those formed by the same salt in the mixture at corresponding concentrations as the amount of water present as solvent in the mixture—the difference between this and the lowering found experimentally becomes increasingly large. This has been discussed in the preceding case.

The method of calculating the composition of the hydrates existing in a mixture of two salts with about the same hydrating power, such as calcium chloride and magnesium chloride, was based upon the assumption that the values of  $M$  in their separate solutions represent the relative hydrating powers under the same conditions for the two salts in their mixtures. While this applies where the hydrates formed are of approximately the same degree of complexity, it would involve an error in the case of two salts of very different hydrating powers. For, if the power of forming hydrates, *i. e.*, of eliminating water from the sphere of action as solvent, differs, then, when two such substances are mixed, if a decrease in the amount of water eliminated from the sphere of action as solvent occurs, this decrease must be assigned to the two salts inversely as their values of  $M$  in separate solutions. This follows from a consideration of the fact that the salt with greater hydrating power will have, consequently, greater power of dehydrating the salt with lesser hydrating power. Therefore, the salt which has less power to unite with water must suffer the greater loss in water of hydration in the presence of the salt with stronger hydrating power.

Upon this assumption the following method of calculating the approximate composition of the hydrates in such a mixture has been worked out: Take the case of a mixture consisting of one volume of 0.3 N strontium chloride and one volume of 0.3 N calcium chloride.

Let  $X$  equal the total decrease in the number of grams of water eliminated from the sphere of action as solvent in the mixture, as compared with that eliminated in the separate solutions.

Then  $\frac{39}{99} X$  = diminution in number of grams of water eliminated by calcium chloride, and  $\frac{60}{99} X$  = diminution in number of grams of water eliminated by strontium chloride (see tables 9 and 15 for the values of  $M$  in separate solutions).

108.5 grams of water were eliminated by the calcium chloride as water of hydration in the 0.15 N separate solution of that salt (see table 9). 70.5 grams were eliminated by the strontium chloride (see table 15). Therefore,

$$108.5 - 0.39X = 1000 - \frac{4186}{L'_{Ca}} \quad (1)$$

$$70.5 - 0.61X = 1000 - \frac{4461}{L'_{Sr}} \quad (2)$$

$$L'_{Ca} = \frac{4186}{891.5 + 0.39X}, \text{ and } L'_{Sr} = \frac{4461}{929.5 + 0.61X}$$

Let  $L'_0$  = observed lowering for calcium chloride in the mixture; then,

$$L'_0 = \frac{4186 \times 0.15}{891.5 + 0.39X} \div \frac{922.5 + 0.61X}{1000} \quad (3)$$

$$1.503 - L'_0 = \frac{4461 \times 0.15}{929.5 + 0.61X} \div \frac{884.5 + 0.39X}{1000} \quad (4)$$

Combining equations (3) and (4),

$$1.503 = \frac{4186 \times 0.15}{822 + 0.904X + 0.0002379X^2} + \frac{4461 \times 0.15}{822 + 0.902X + 0.0002379X^2}$$

From this equation the approximate value of  $X$  can be obtained. The values of  $M$  and  $H$  for the mixture of calcium chloride and strontium chloride, thus obtained, are given in table 18. The symbols have the usual significance.

TABLE 18.—*Hydration in the Mixtures of Calcium Chloride and Strontium Chloride.*

$m$	$m_c$	$a$	$L_c$	$M$	$\Delta$	Sp. gr. cor.	$M_c$	$H_c$
0.3 CaCl <sub>2</sub> .....	0.15	0.625	4.186	6.0)	1.503	0.7	{ 5.1	34.0
0.3 SrCl <sub>2</sub> .....	0.15	0.699	4.461	3.9)			{ 2.4	16.0
0.5 CaCl <sub>2</sub> .....	0.25	0.590	4.056	8.2)	2.626	1.1	{ 7.3	29.2
0.5 SrCl <sub>2</sub> .....	0.25	0.647	4.266	5.5)			{ 4.2	16.8
0.7 CaCl <sub>2</sub> .....	0.35	0.560	3.942	9.7)	3.906	1.6	{ 9.3	26.1
0.7 SrCl <sub>2</sub> .....	0.35	0.610	4.127	7.1)			{ 6.5	18.6
0.9 CaCl <sub>2</sub> .....	0.45	0.519	3.791	11.7)	5.310	2.2	{ 11.1	24.7
0.9 SrCl <sub>2</sub> .....	0.45	0.583	4.030	9.0)			{ 8.3	18.2
1.3 CaCl <sub>2</sub> .....	0.65	0.461	3.576	15.7)	8.682	3.3	{ 15.1	23.2
1.3 SrCl <sub>2</sub> .....	0.65	0.521	3.797	12.4)			{ 11.6	17.8
1.7 CaCl <sub>2</sub> .....	0.85	0.408	3.378	18.9)	12.924	4.4	{ 18.3	21.5
1.7 SrCl <sub>2</sub> .....	0.85	0.466	3.593	15.7)			{ 15.0	17.6
2.1 CaCl <sub>2</sub> .....	1.05	0.352	3.171	21.9)	18.290	5.6	{ 21.5	20.5
2.1 SrCl <sub>2</sub> .....	1.05	0.414	3.400	18.7)			{ 18.2	17.3

For the sake of comparison, the values of  $M$  for the separate solutions of calcium chloride and strontium chloride and those for the mixture of the two salts have been plotted as curves in fig. 4.

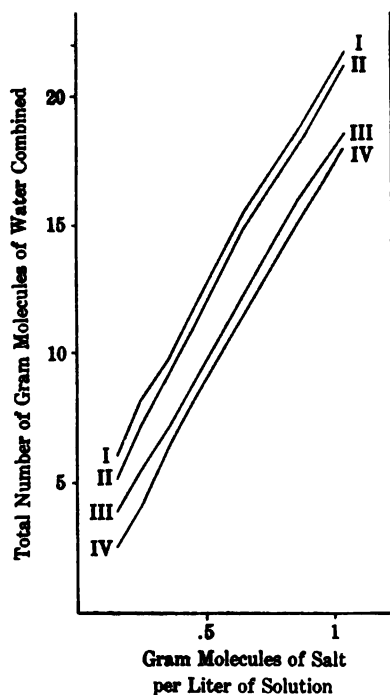


FIG. 4.

- I. Calcium Chloride Alone.
- II. Calcium Chloride Mixed with Strontium Chloride.
- III. Strontium Chloride Alone.
- IV. Strontium Chloride Mixed with Calcium Chloride

We find that the results expressed in fig. 4 are of the same character as those shown in fig. 3 for the mixture of calcium chloride and magnesium chloride. The curve of hydration of each salt in the mixture is parallel to the curve of its hydration in the single solution, except where large values, as shown in curve I, for calcium chloride alone have produced a corresponding lessening in the amount of water with which the strontium chloride has been able to unite in the mixture at a normality of 0.15 to 0.35. An increase in the hydrating power of the calcium chloride must necessarily be accompanied by a corresponding decrease in the complexity of the hydrates of strontium chloride.

TABLE 19.—Difference in Amount of Water Present as Solvent in Separate Solutions and in Mixtures.

$m$ .	Calcium chloride in mixture of calcium chloride and strontium chloride.		Strontium chloride in mixture of calcium chloride and strontium chloride.	
	$D_{H_2O}$	$D_m$	$D_{H_2O}$	$D_m$
0.15	46	0.9	96	1.5
0.25	81	0.9	137	1.3
0.35	127	0.4	176	0.6
0.45	162	0.6	212	0.7
0.65	226	0.6	289	0.8
0.85	295	0.6	353	0.7
1.05	359	0.4	419	5.0

In order to compare the difference in the amount of water present as solvent in the single solution and in the mixture with the difference in the value of  $M$  in the two cases, these values are tabulated. (Table 19.)  $D_{H_2O}$  is the difference in the amount of water present as solvent in the separate solution and in the mixture. It is found for a given salt by adding to the number of grams of water eliminated as water of hydration by the other salts in the mixture, the difference between the correction to weight-normal standard in the case of the separate solution of the salt in question and in the mixture.  $D_m$  is the difference between the value of  $M$  in the single solution and in the mixture. These values are plotted as curves in figs. 5 and 6. The concentrations are the abscissæ, and for curve I the grams of water are taken as ordinates. In curve II gram-molecules of water form the ordinates.

FIG. 5.

- I. Difference between Water Present as Solvent in Single Solution of Calcium Chloride and in Mixture of Calcium Chloride and Strontium Chloride.
- II. Difference between the Values of  $M$  for Calcium Chloride in Single Solution and in the Mixture of Calcium Chloride and Strontium Chloride.

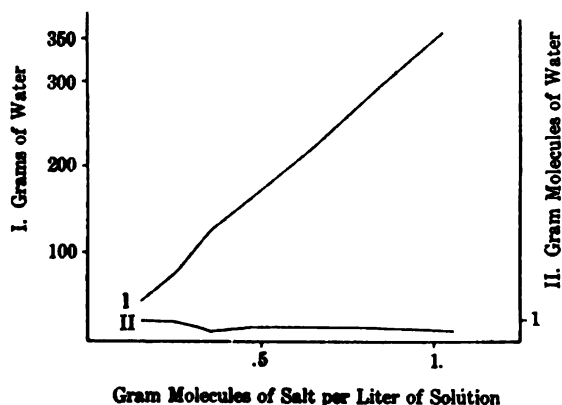
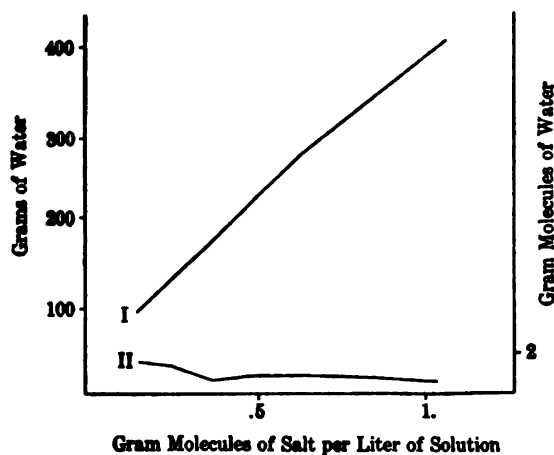


FIG. 6.

- I. Difference between Water Present as Solvent in Single Solution of Strontium Chloride and in Mixture of Calcium Chloride and Strontium Chloride.
- II. Difference between the Values of  $M$  for Strontium Chloride in Single Solution and in the Mixture of Calcium Chloride and Strontium Chloride.



It is readily seen from a comparison of the curves that the decrease in the amount of water present as solvent in the mixture is not accompanied by a corresponding decrease in the values of  $M$ . Here again, as in the case of the mixture of calcium chloride and potassium chloride, the difference in the values of  $M$  is nearly constant, because the concentration of both salts present in the mixture is increased at the same rate. Slight changes might be manifest if the ions and molecules have different



hydrating powers, as seems very probable. Then a decrease in the number of ions and a correspondingly large increase in the number of molecules of dissolved substance present, such as necessarily occurs owing to suppression of the ionization in the mixture, would be accompanied by a change in the number of grams of water combined. That this plays a part in the change noted seems very probable.

For purposes of comparison these same values are given in table 20 for a few concentrations in the case of calcium chloride and magnesium chloride. The phenomena are of the same kind.

TABLE 20.—*Mixtures of Calcium Chloride and Magnesium Chloride.*

<i>m</i>	Calcium chloride in calcium chloride and magnesium chloride mixture.		Magnesium chloride in calcium chloride and magnesium chloride mixture.	
	<i>DH<sub>2</sub>O</i>	<i>D<sub>m</sub></i>	<i>DH<sub>2</sub>O</i>	<i>D<sub>m</sub></i>
0.65	310.2	1.2	279	1.4
0.85	373.8	1.8	333	2.1
1.05	435.0	2.1	389	2.4
1.25	507.0	1.5	450	1.8
1.45	562.2	1.4	512	2.0

## MAGNESIUM NITRATE AND STRONTIUM NITRATE.

A pair of nitrates was next studied.

The salts must be of such a nature as not to unite to form complexes when mixed, and must have hydrating power. Magnesium nitrate and strontium nitrate were selected. The data for these two salts are given in tables 21 to 23.

TABLE 21.—*Magnesium Nitrate—Data for Freezing-point and Conductivity Measurements, Weight-normal Corrections, and Hydrates.*

<i>m</i>	Freezing-point.		Hydrates.				
	$\Delta$	$\Delta/m$	<i>a</i>	<i>L</i>	<i>L'</i>	<i>M</i>	<i>H</i>
0.15	0.749	4.99	0.711	4.50	4.97	5.3	35.1
0.25	1.252	5.01	0.671	4.36	4.96	6.7	26.9
0.35	1.805	5.16	0.636	4.23	5.09	9.4	26.8
0.45	2.395	5.32	0.607	4.12	5.22	11.7	26.0
0.55	3.019	5.49	0.587	4.05	5.36	13.6	24.7
0.65	3.669	5.64	0.562	3.95	5.49	15.6	24.0
0.75	4.393	5.86	0.542	3.88	5.68	17.6	23.5

<i>m</i>	Conductivity.			Weight-normal corrections.			
	<i>V</i>	<i>k</i>	$\mu_0$	<i>W<sub>sol</sub></i>	<i>W<sub>salt</sub></i>	<i>W<sub>H<sub>2</sub>O</sub></i>	Correction, per cent.
0.15	6.6666	0.01370	91.3	25.4306	0.5567	24.8738	0.5
0.25	4.0000	0.02156	86.3	25.6880	0.9277	24.7603	1.0
0.35	2.8571	0.02861	81.8	25.9782	1.2989	24.6794	1.3
0.45	2.2222	0.03512	78.1	26.2075	1.6610	24.5376	1.8
0.55	1.8182	0.04151	75.5	26.4748	2.0411	24.4338	2.3
0.65	1.5380	0.04604	72.2	26.7605	2.4122	24.3484	2.6
0.75	1.3333	0.05226	69.7	27.0203	2.7833	24.2371	3.1

TABLE 22.—*Strontium Nitrate—Data for Freezing-point and Conductivity Measurements, Weight-normal Corrections, and Hydrates.*

<i>m</i>	Freezing-point.		Hydrates.				
	$\Delta$	$\Delta/m$	<i>a</i>	<i>L</i>	<i>L'</i>	<i>M</i>	<i>H</i>
0.15	0.674	4.49	0.653	4.29	4.46	2.1	14.1
0.25	1.085	4.34	0.592	4.06	4.29	2.98	11.9
0.35	1.516	4.33	0.548	3.80	4.25	4.6	13.2
0.45	1.903	4.23	0.507	3.75	4.13	5.1	11.4
0.55	2.286	4.16	0.475	3.63	4.04	5.6	10.3
0.65	2.681	4.12	0.446	3.52	3.98	6.4	9.9
0.75	3.060	4.08	0.417	3.41	3.92	7.2	9.6

<i>m</i>	Conductivity.			Weight-normal corrections.			
	<i>V</i>	<i>k</i>	$\mu_e$	<i>W<sub>sol</sub></i>	<i>W<sub>salt</sub></i>	<i>W<sub>H<sub>2</sub>O</sub></i>	Correction, per cent.
0.15	6.6666	0.01316	87.8	25.6245	0.7938	24.8307	0.7
0.25	4.0000	0.01990	79.6	26.0440	1.3542	24.6898	1.2
0.35	2.8571	0.02575	73.6	26.4408	1.8960	24.5449	1.8
0.45	2.2222	0.03064	68.1	26.8623	2.4376	24.4247	2.3
0.55	1.8182	0.03511	63.8	27.2890	2.9793	24.3097	2.8
0.65	1.5380	0.03894	59.9	27.0907	3.5210	24.1697	3.3
0.75	1.3333	0.04207	56.1	28.0818	4.0627	24.0191	3.9

TABLE 23.—*Mixture of Magnesium Nitrate and Strontium Nitrate—Data for Freezing-point and Conductivity Measurements, Weight-normal Corrections, and Hydrates.*

<i>m</i>	Weight-normal corrections.				Fr.-pt.
	<i>W<sub>sol</sub></i>	<i>W<sub>salt</sub></i>	<i>W<sub>H<sub>2</sub>O</sub></i>	Correction, per cent.	Δ
0.3 Mg(NO <sub>3</sub> ) <sub>2</sub> +0.3 Sr(NO <sub>3</sub> ) <sub>2</sub> .....	26.044	1.3505	24.6936	1.2	1.394
0.5 Mg(NO <sub>3</sub> ) <sub>2</sub> +0.5 Sr(NO <sub>3</sub> ) <sub>2</sub> .....	26.7087	2.2819	24.4268	2.3	2.351
0.7 Mg(NO <sub>3</sub> ) <sub>2</sub> +0.7 Sr(NO <sub>3</sub> ) <sub>2</sub> .....	27.3970	3.1948	24.2022	3.2	3.371
0.9 Mg(NO <sub>3</sub> ) <sub>2</sub> +0.9 Sr(NO <sub>3</sub> ) <sub>2</sub> .....	28.0570	4.1076	23.9435	4.2	4.573
1.1 Mg(NO <sub>3</sub> ) <sub>2</sub> +1.1 Sr(NO <sub>3</sub> ) <sub>2</sub> .....	28.6884	5.0208	23.6681	5.3	5.646
1.3 Mg(NO <sub>3</sub> ) <sub>2</sub> +1.3 Sr(NO <sub>3</sub> ) <sub>2</sub> .....	29.3508	5.9332	23.4177	6.3	6.893
1.5 Mg(NO <sub>3</sub> ) <sub>2</sub> +1.5 Sr(NO <sub>3</sub> ) <sub>2</sub> .....	29.9912	6.8460	23.1452	7.4	8.169

Conductivity.								
<i>m</i>	<i>m<sub>c</sub></i>	<i>V<sub>c</sub></i>	<i>k<sub>s</sub></i>	<i>k</i>	<i>D</i>	<i>k<sub>c</sub></i>	<i>μ<sub>g</sub></i>	<i>a</i>
0.3 Mg(NO <sub>3</sub> ) <sub>2</sub> ....	0.15	6.6666	0.02384	{0.01370}	0.00302	{0.01229}	81.9	0.638
0.3 Sr(NO <sub>3</sub> ) <sub>2</sub> ....	0.15	6.6666		{0.01316}		{0.01155}	77.0	0.573
0.5 Mg(NO <sub>3</sub> ) <sub>2</sub> ....	0.25	4.0000	0.03552	{0.02156}	0.00595	{0.01884}	75.4	0.587
0.5 Sr(NO <sub>3</sub> ) <sub>2</sub> ....	0.25	4.0000		{0.01990}		{0.01668}	66.7	0.497
0.7 Mg(NO <sub>3</sub> ) <sub>2</sub> ....	0.35	2.8571	0.04466	{0.02861}	0.00970	{0.02423}	69.2	0.539
0.7 Sr(NO <sub>3</sub> ) <sub>2</sub> ....	0.35	2.8571		{0.02575}		{0.02043}	58.4	0.434
0.9 Mg(NO <sub>3</sub> ) <sub>2</sub> ....	0.45	2.2222	0.05170	{0.03512}	0.01406	{0.02888}	64.2	0.500
0.9 Sr(NO <sub>3</sub> ) <sub>2</sub> ....	0.45	2.2222		{0.03064}		{0.02283}	50.7	0.378
1.1 Mg(NO <sub>3</sub> ) <sub>2</sub> ....	0.55	1.8182	0.05707	{0.04151}	0.01953	{0.03299}	60.0	0.467
1.1 Sr(NO <sub>3</sub> ) <sub>2</sub> ....	0.55	1.8182		{0.03511}		{0.02410}	43.8	0.326
1.3 Mg(NO <sub>3</sub> ) <sub>2</sub> ....	0.65	1.538	0.06100	{0.04694}	0.02488	{0.03620}	55.7	0.433
1.3 Sr(NO <sub>3</sub> ) <sub>2</sub> ....	0.65	1.538		{0.03894}		{0.02479}	38.1	0.284
1.5 Mg(NO <sub>3</sub> ) <sub>2</sub> ....	0.75	1.3333	0.06379	{0.05226}	0.03055	{0.03931}	52.4	0.408
1.5 Sr(NO <sub>3</sub> ) <sub>2</sub> ....	0.75	1.3333		{0.04208}		{0.02445}	32.6	0.243

TABLE 23—Continued.

Hydrates.						
<i>m</i>	<i>L<sub>c</sub></i>	<i>M</i>	$\Delta$	Sp. gr. cor.	<i>M<sub>c</sub></i>	<i>H<sub>c</sub></i>
0.3 Mg(NO <sub>3</sub> ) <sub>2</sub> .....	4.231	5.3	1.394	1.2	4.9	32.5
0.3 Sr(NO <sub>3</sub> ) <sub>2</sub> .....	3.992	2.1			1.0	6.6
0.5 Mg(NO <sub>3</sub> ) <sub>2</sub> .....	4.042	6.7	2.351	2.3	6.5	26.0
0.5 Sr(NO <sub>3</sub> ) <sub>2</sub> .....	3.707	3.0			2.4	9.6
0.7 Mg(NO <sub>3</sub> ) <sub>2</sub> .....	3.864	9.4	3.371	3.2	8.8	25.1
0.7 Sr(NO <sub>3</sub> ) <sub>2</sub> .....	3.476	4.6			3.4	9.6
0.9 Mg(NO <sub>3</sub> ) <sub>2</sub> .....	3.718	11.7	4.583	4.2	11.4	25.3
0.9 Sr(NO <sub>3</sub> ) <sub>2</sub> .....	3.264	5.1			4.4	9.8
1.1 Mg(NO <sub>3</sub> ) <sub>2</sub> .....	3.596	13.6	5.646	5.3	13.3	24.2
1.1 Sr(NO <sub>3</sub> ) <sub>2</sub> .....	3.073	5.6			4.9	8.8
1.3 Mg(NO <sub>3</sub> ) <sub>2</sub> .....	3.472	15.6	6.892	6.3	15.2	23.4
1.3 Sr(NO <sub>3</sub> ) <sub>2</sub> .....	2.915	6.4			5.5	8.5
1.5 Mg(NO <sub>3</sub> ) <sub>2</sub> .....	3.377	17.6	8.169	7.4	17.0	22.7
1.5 Sr(NO <sub>3</sub> ) <sub>2</sub> .....	2.763	7.2			5.7	7.6

The values of *M* for this mixture are calculated by the method already given. Evidently the same method of calculation applies here as in the case of a mixture of calcium chloride and strontium chloride.

The values of *M*, in single solution and in the mixture, for magnesium nitrate and strontium nitrate have been plotted as curves in fig. 7. The phenomena are, in gen-

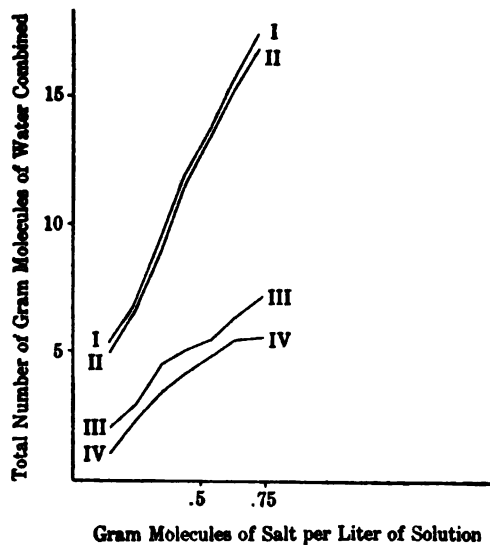


FIG. 7.

- I. Magnesium Nitrate Alone.
- II. Magnesium Nitrate Mixed with Strontium Nitrate.
- III. Strontium Nitrate Alone.
- IV. Strontium Nitrate Mixed with Magnesium Nitrate.

eral, the same as those already pointed out in preceding cases. Curve IV deviates from curve III with increasing concentration, showing the effect of the large increase in the value of *M* for magnesium nitrate, with increasing concentration, upon the amount of water eliminated as water of hydration by the strontium nitrate. The strontium nitrate is dehydrated, partially, by the magnesium nitrate.

In table 24 we have the differences in the amount of solvent present and in the values of  $M$ , as previously described for the corresponding tables. In figs. 8 and 9 these values are plotted as curves.

TABLE 24.—Differences in Amount of Solvent Present—Mixtures of Magnesium Nitrate and Strontium Nitrate.

$m$	Magnesium nitrate in mixture of magnesium nitrate and strontium nitrate.		Strontium nitrate in mixture of magnesium nitrate and strontium nitrate.	
	$DH_2O$	$D_m$	$DH_2O$	$D_m$
0.15	25	0.4	93	1.1
0.25	56	0.2	128	0.6
0.35	80	0.6	172	1.3
0.45	103	0.3	224	0.7
0.55	118	0.3	264	0.7
0.65	136	0.4	304	0.9
0.75	146	0.6	341	1.5

FIG. 8.

- I. Difference between Water Present as Solvent in Single Solution of Magnesium Nitrate and in Mixture of Magnesium Nitrate and Strontium Nitrate.
- II. Difference between Values of  $M$  for Magnesium Nitrate in Single Solution and in Mixture of Magnesium Nitrate and Strontium Nitrate.

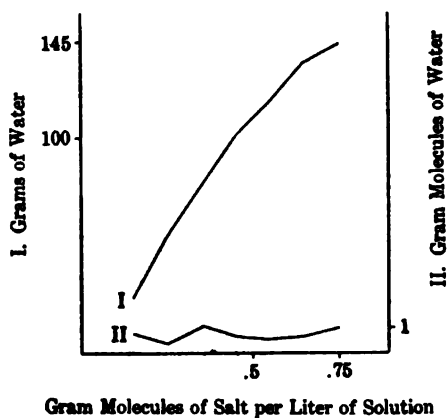
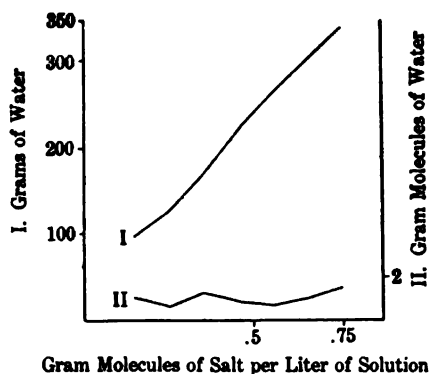


FIG. 9.

- I. Difference between Water Present as Solvent in Single Solution of Strontium Nitrate and in the Mixture of Magnesium Nitrate and Strontium Nitrate.
- II. Difference between Values of  $M$  for Strontium Nitrate in Single Solution and in Mixture of Magnesium Nitrate and Strontium Nitrate.



We have here, again, a uniform decrease in the amount of water present as solvent, showing a uniform increase in the hydration with increase in concentration. The

curves showing the differences in the values of  $M$  correspond to a constant difference in the amount of water eliminated in single solution and in the mixture. This constant difference is, of course, due to the fact that the concentration of both salts in the mixture is increased uniformly. The curves show, also, that this difference is slightly affected by the difference in the amount of water present as solvent, since they show a tendency to increase as the diminution in water present as solvent becomes greater.

#### SODIUM BROMIDE AND LITHIUM BROMIDE.

We next took up a pair of binary electrolytes, *lithium bromide* and *sodium bromide*, neither of which has a very large hydrating power, the hydrating power of the sodium bromide being somewhat less than that of the lithium bromide. (Tables 25 and 26.)

TABLE 25.—*Sodium Bromide—Data for Freezing-point and Conductivity Measurements, Weight-normal Corrections, and Hydrates.*

$m$	Freezing-point.		Hydrates.				
	$\Delta$	$\Delta/m$	$a$	$L$	$L'$	$M$	$H$
0.25	0.895	3.58	0.845	3.43	3.55	1.9	7.6
0.35	1.249	3.57	0.828	3.40	3.54	2.2	6.3
0.45	1.601	3.56	0.815	3.38	3.52	2.2	4.9
0.55	1.946	3.54	0.799	3.35	3.49	2.2	4.0
0.65	2.298	3.54	0.779	3.31	3.48	2.7	4.2
0.75	2.691	3.59	0.774	3.30	3.52	3.5	4.6
0.85	3.054	3.59	0.765	3.28	3.51	3.6	4.2
0.95	3.435	3.62	0.760	3.27	3.53	4.1	4.3
1.05	3.839	3.66	0.747	3.25	3.56	4.8	4.6

$m$	Conductivity.			Weight-normal corrections.			
	$V$	$k$	$\mu_0$	$W_{sat}$	$W_{sat}$	$WH_2O$	Correction, per cent.
0.25	4.0000	0.01431	57.2	25.4629	0.6438	24.8191	0.4
0.35	2.8571	0.01963	56.1	25.7300	0.9014	24.7987	0.8
0.45	2.2222	0.02484	55.2	25.8823	1.1589	24.7234	1.1
0.55	1.8182	0.02974	54.1	26.0735	1.4164	24.6571	1.4
0.65	1.5380	0.03427	52.7	26.2560	1.6727	24.5833	1.7
0.75	1.3333	0.03932	52.4	26.4535	1.9344	24.5221	1.9
0.85	1.1765	0.04401	51.8	26.6155	2.1890	24.4265	2.3
0.95	1.0526	0.04885	51.4	26.8260	2.4465	24.3795	2.5
1.05	0.9523	0.05323	50.7	27.0072	2.7040	24.3032	2.8

Since lithium bromide and sodium bromide are each binary and dissociated to almost exactly the same extent at equal concentrations of the solutions, the loss in conductivity is apportioned to an equal driving back in the dissociation of the lithium bromide and sodium bromide, except in the mixtures  $\left. \begin{array}{l} 1.7 \text{ LiBr} \\ 1.7 \text{ NaBr} \end{array} \right\}$  and  $\left. \begin{array}{l} 1.9 \text{ LiBr} \\ 1.9 \text{ NaBr} \end{array} \right\}$ , where the slight difference in the dissociation of the separate solutions is taken into account.

TABLE 26.—*Lithium Bromide—Data for Freezing-point and Conductivity Measurements, Weight-normal Corrections, and Hydrates.*

<i>m</i>	Freezing-point.		Hydrates.				
	$\Delta$	$\Delta/m$	$\alpha$	<i>L</i>	<i>L'</i>	<i>M</i>	<i>H</i>
0.25	0.917	3.67	0.848	3.44	3.65	3.2	12.8
0.35	1.292	3.69	0.825	3.39	3.63	3.7	10.6
0.45	1.679	3.75	0.805	3.36	3.71	5.2	11.6
0.45	1.679	3.75	0.785	3.32	3.75	6.4	11.6
0.65	2.514	3.87	0.757	3.29	3.81	7.5	11.5
0.75	2.957	3.94	0.745	3.27	3.87	8.6	11.5
0.85	3.418	4.02	0.734	3.25	3.94	9.7	11.4
0.95	3.900	4.11	0.723	3.23	4.01	10.8	11.4
1.05	4.381	4.17	0.767	3.21	4.06	11.6	11.0

<i>m</i>	Conductivity.			Weight-normal corrections.			
	<i>V</i>	<i>k</i>	$\mu_0$	<i>W<sub>sol</sub></i>	<i>W<sub>salt</sub></i>	<i>W<sub>H<sub>2</sub>O</sub></i>	Correction, per cent.
0.25	4.0000	0.01270	50.8	25.3913	0.5437	24.8476	0.6
0.35	2.8571	0.01729	49.4	25.5641	0.7612	24.8029	0.8
0.45	2.2222	0.02169	48.2	25.7225	0.9786	24.7439	1.0
0.55	1.8182	0.02585	47.0	25.8690	1.1961	24.6729	1.3
0.65	1.5380	0.02986	45.0	26.0358	1.4136	24.6222	1.5
0.75	1.3333	0.03400	45.3	26.1585	1.6311	24.5274	1.9
0.85	1.1765	0.05790	44.6	26.3303	1.8485	24.4818	2.1
0.95	1.0526	0.04176	44.0	26.4558	2.0660	24.3898	2.4
1.05	0.9523	0.04550	43.3	26.6235	2.2835	24.3400	2.6

The values of *M* and *H* for this mixture are calculated upon the same basis as that previously employed in the mixture of magnesium nitrate and strontium nitrate. The values thus obtained for the mixture of lithium bromide and sodium bromide are given in table 27.

TABLE 27.—*Mixture of Lithium Bromide and Sodium Bromide—Data for Weight-normal Corrections, Freezing-point and Conductivity Measurements, and Hydrates.*

<i>m</i>	Weight-normal corrections.				Fr.-pt.
	<i>W<sub>sol</sub></i>	<i>W<sub>salt</sub></i>	<i>W<sub>H<sub>2</sub>O</sub></i>	Correction, per cent.	$\Delta$
0.5 LiBr+0.5 NaBr.....	25.9003	1.1875	24.7128	1.1	1.823
0.7 LiBr+0.7 NaBr.....	26.2462	1.6625	24.5837	1.7	2.596
0.9 LiBr+0.9 NaBr.....	26.6053	2.1375	24.4678	2.1	3.415
1.1 LiBr+1.1 NaBr.....	26.9317	2.6125	24.3192	2.7	4.325
1.3 LiBr+1.3 NaBr.....	27.2984	3.0863	24.2121	3.2	5.284
1.5 LiBr+1.5 NaBr.....	27.5978	3.5625	24.0353	3.9	6.293
1.7 LiBr+1.7 NaBr.....	27.9400	4.0375	23.9025	4.4	7.328
1.9 LiBr+1.9 NaBr.....	28.2890	4.5125	23.7765	4.9	8.399
2.1 LiBr+2.1 NaBr.....	28.6065	4.9875	23.6190	5.5	9.539

TABLE 27—Continued.

Conductivity.								
$m$	$m_c$	$V_c$	$k_u$	$k$	$D$	$k_c$	$\mu_0$	$a$
0.5 LiBr.....	0.25	4.0000	0.02549	0.01270	0.00152	0.01199	47.9	0.800
0.5 NaBr.....	0.25	4.0000		0.01431		0.00135	54.0	0.798
0.7 LiBr.....	0.35	2.8571	0.03433	0.01729	0.00259	0.01607	45.9	0.767
0.7 NaBr.....	0.35	2.8571		0.01963		0.01825	52.2	0.770
0.9 LiBr.....	0.45	2.2222	0.04273	0.02169	0.00381	0.01990	44.2	0.738
0.9 NaBr.....	0.45	2.2222		0.02484		0.02282	50.7	0.749
1.1 LiBr.....	0.55	1.8182	0.05110	0.02585	0.00449	0.02374	43.2	0.721
1.1 NaBr.....	0.55	1.8182		0.02974		0.02736	49.8	0.735
1.3 LiBr.....	0.65	1.5380	0.05894	0.02986	0.00519	0.02725	42.2	0.704
1.3 NaBr.....	0.65	1.5380		0.03427		0.03152	48.5	0.716
1.5 LiBr.....	0.75	1.3333	0.06649	0.03790	0.00683	0.03079	41.1	0.685
1.5 NaBr.....	0.75	1.3333		0.04401		0.03570	47.6	0.703
1.7 LiBr.....	0.85	1.1765	0.07313	0.04176	0.00879	0.03384	39.8	0.665
1.7 NaBr.....	0.85	1.1765		0.04885		0.03930	46.2	0.683
1.9 LiBr.....	0.95	1.0526	0.08041	0.04550	0.01020	0.03699	38.8	0.648
1.9 NaBr.....	0.95	1.0526		0.05323		0.04353	45.8	0.677
2.1 LiBr.....	1.05	0.9523	0.08665	0.03400	0.01209	0.03983	37.9	0.633
2.1 NaBr.....	1.05	0.9523		0.03932		0.04681	44.6	0.659

Hydrates.					
$m$	$L_c$	$M$	Sp. gr. cor.	$M_c$	$H_c$
0.5 LiBr.....	3.349	3.2	1.1	2.8	11.2
0.5 NaBr.....	3.344	1.9		1.2	4.8
0.7 LiBr.....	3.286	3.7	1.7	3.5	10.0
0.7 NaBr.....	3.293	2.2		2.0	15.7
0.9 LiBr.....	3.233	5.2	2.1	5.2	11.5
0.9 NaBr.....	3.263	2.2		2.0	4.5
1.1 LiBr.....	3.201	6.4	2.7	6.7	12.2
1.1 NaBr.....	3.227	2.2		2.3	4.2
1.3 LiBr.....	3.107	7.5	3.2	8.0	12.3
1.3 NaBr.....	3.192	2.7		2.9	4.5
1.5 LiBr.....	3.135	8.6	3.9	8.9	11.8
1.5 NaBr.....	3.168	3.5		3.6	4.8
1.7 LiBr.....	3.096	9.7	4.4	10.2	12.0
1.7 NaBr.....	3.130	3.6		3.8	4.4
1.9 LiBr.....	3.065	10.8	4.9	11.0	11.6
1.9 NaBr.....	3.119	4.1		4.2	4.4
2.1 LiBr.....	3.038	11.6	5.5	11.6	11.0
2.1 NaBr.....	3.085	4.8		4.8	4.6

Curve II, fig. 10, representing the value of  $M$  in the mixture of lithium bromide and sodium bromide, crosses curve I, the value of  $M$  for lithium bromide in single solution. The same phenomenon presents itself in the case of sodium bromide at a somewhat greater concentration. In an earlier part of this investigation it was suggested that the hydrating power of the ions alone, and of these ions when combined to form molecules, would probably be different. If, now, the hydrating power of the lithium bromide and the sodium bromide molecules is greater than that of the respective ions, we might expect that the effect of the smaller amount of water present as solvent in the mixture would be overcome by the greater hydrating power of the undissociated molecules. Evidently, for this increased hydrating power of the molecules over the

ions to show itself in the resulting curve, the other salt in the mixture must have hydrating power and a comparatively small molecular weight; for if the molecular weight is large so much solvent will be displaced when the solutions are made up volume normal that the decreased amount of solvent will obscure any change in hydration due to other causes. Also, the difference in the hydrating power of the ions and molecules should be considerable, in order to overcome the effect of decrease in amount of solvent present with increase in concentration.

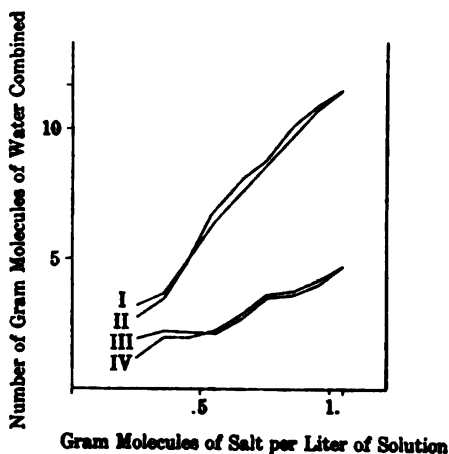


FIG. 10.

- I. Lithium Bromide Alone.  
 II. Lithium Bromide Mixed with Sodium Bromide.  
 III. Sodium Bromide Alone.  
 IV. Sodium Bromide Mixed with Lithium Bromide.

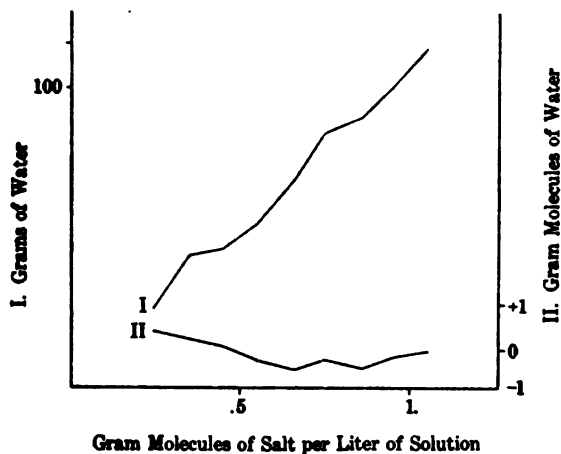


FIG. 11.

- I. Difference between Amount of Water Present as Solvent in Single Solution of Lithium Bromide and in Mixture of Lithium Bromide and Sodium Bromide.  
 II. Difference between Values of  $M$  for Lithium Bromide in Single Solution and in Mixture of Lithium Bromide and Sodium Bromide.

The difference between the amount of water acting as solvent towards each salt in the mixture and in single solution, and the differences between the values of  $M$  in the same cases, are given in table 28. A negative value of  $D_m$  indicates that the number of grams of water eliminated by a salt in a mixture is greater, instead of less, than in single solution.

TABLE 28.

$m$	Lithium bromide in mixture of lithium bromide and sodium bromide.		Sodium bromide in mixture of lithium bromide and sodium bromide.	
	$D_{H_2O}$	$D_m$	$D_{H_2O}$	$D_m$
0.25	27	0.4	54	0.7
0.35	45	0.2	72	0.2
0.45	47	0.0	104	0.2
0.55	55	-0.3	134	-0.1
0.65	69	-0.5	159	-0.2
0.75	85	-0.3	180	-1.1
0.85	91	-0.3	205	-0.2
0.95	101	-0.2	222	-0.1
1.05	115	0.0	236	0.0



These values are plotted as curves in figs. 11 and 12. The fact that the curves show positive values of  $D_m$  has already been explained as possibly due to the increased hydrating power of the molecule over its ions, so that when sufficient driving back in dissociation occurs we would get an increased amount of water eliminated as water of hydration. That this difference is nearly constant is to be expected, since corresponding additions of sodium bromide and lithium bromide are always made in changes of concentration.

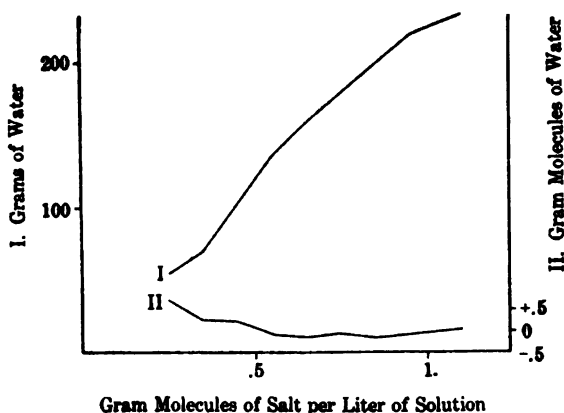


FIG. 12.

- I. Difference between Amount of Water Present as Solvent in Single Solution of Sodium Bromide and in Mixture of Sodium Bromide and Lithium Bromide.
- II. Difference between Values of  $M$  for Sodium Bromide in Single Solution and in Mixture of Sodium Bromide and Lithium Bromide.

#### CALCIUM NITRATE AND MAGNESIUM NITRATE.

The values of  $M$  for each salt in the mixture and in separate solution are plotted as curves in fig. 13. With increased concentration we have increased divergence in curves I and III, which represent the hydrating power (values of  $M$ ) in separate solutions of magnesium nitrate and of calcium nitrate, respectively. Consequently, as we should expect, curves II and IV, representing the values of  $M$  for the two salts in the mixture, show increasing divergence with increase in concentration. The values given in table 32 are plotted as curves in figs. 14 and 15.

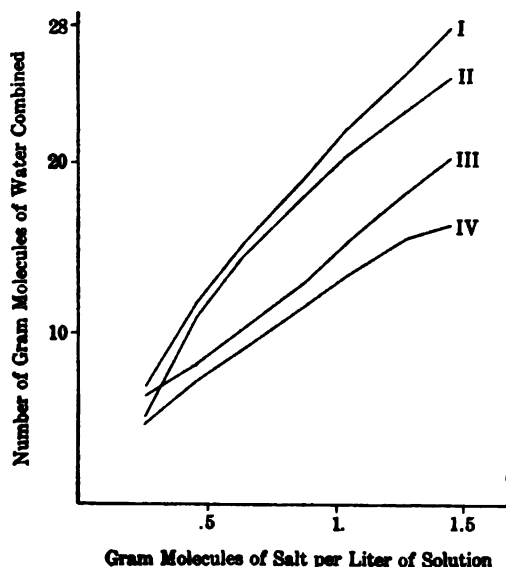


FIG. 13.

- I. Magnesium Nitrate Alone.
- II. Magnesium Nitrate Mixed with Calcium Nitrate.
- III. Calcium Nitrate Alone.
- IV. Calcium Nitrate Mixed with Magnesium Nitrate.

TABLE 29.—*Calcium Nitrate—Data for Freezing-point and Conductivity Measurements, Weight-normal Corrections, and Hydrates.*

<i>m</i>	Freezing-point.		Hydrates.				
	$\Delta$	$\Delta/m$	<i>a</i>	<i>L</i>	<i>L'</i>	<i>M</i>	<i>H</i>
0.25	1.189	4.756	0.624	4.18	4.71	6.3	25.2
0.45	2.094	4.65	0.550	3.90	4.56	8.0	17.9
0.65	3.041	4.68	0.491	3.69	4.55	10.5	16.2
0.85	4.057	4.77	0.440	3.50	4.53	13.1	15.4
1.05	5.123	4.88	0.399	3.34	4.65	15.7	15.0
1.25	6.345	5.08	0.359	3.20	4.79	18.4	14.7
1.45	7.547	5.21	0.324	3.07	4.85	20.4	14.1
1.6555	8.859	5.35	0.291	2.94	4.93	22.4	13.5

<i>m</i>	Conductivity.			Weight-normal corrections.			
	<i>V</i>	<i>k</i>	$\mu_v$	<i>W<sub>sol</sub></i>	<i>W<sub>sat</sub></i>	<i>W<sub>H<sub>2</sub>O</sub></i>	Correction, per cent.
0.25	4.0000	0.02097	83.9	25.7766	1.0260	24.7405	1.0
0.45	2.2222	0.03326	73.9	26.3748	1.8467	24.5281	1.9
0.65	1.5380	0.04293	66.0	26.9693	2.6674	24.3019	2.8
0.85	1.1765	0.05027	59.2	27.5168	3.4882	24.2860	3.9
1.05	0.9525	0.05630	53.6	28.1060	4.3089	23.7971	4.8
1.25	0.8000	0.06036	48.3	28.6822	5.1297	23.5525	5.8
1.45	0.6897	0.06324	43.6	29.2340	5.9504	23.2836	6.9
1.6555	0.6041	0.06467	39.1	29.8480	6.7938	23.0542	7.8

TABLE 30.—*Magnesium Nitrate—Data for Freezing-point and Conductivity Measurements, Weight-normal Corrections, and Hydrates.*

<i>m</i>	Freezing-point.		Hydrates.				
	$\Delta$	$\Delta/m$	<i>a</i>	<i>L</i>	<i>L'</i>	<i>M</i>	<i>H</i>
0.25	1.252	5.01	0.671	4.36	4.96	6.7	26.8
0.45	2.395	5.32	0.607	4.12	5.22	11.7	26.0
0.65	3.669	5.64	0.562	3.95	5.49	15.6	24.0
0.85	5.113	6.02	0.520	3.80	5.79	19.1	22.5
1.05	6.762	6.44	0.484	3.66	6.13	22.4	21.3
1.25	8.562	6.85	0.446	3.52	6.47	25.3	20.2
1.45	10.589	7.30	0.409	3.38	6.83	28.1	19.4

<i>m</i>	Conductivity.			Weight-normal corrections.			
	<i>V</i>	<i>k</i>	$\mu_v$	<i>W<sub>sol</sub></i>	<i>W<sub>sat</sub></i>	<i>W<sub>H<sub>2</sub>O</sub></i>	Correction, per cent.
0.25	4.0000	0.02156	86.3	25.6880	0.9277	24.7603	1.0
0.45	2.2222	0.03512	78.1	26.2075	1.6699	24.5376	1.8
0.65	0.5380	0.04694	72.2	26.7605	2.4122	24.3483	2.6
0.85	1.1765	0.05682	66.9	27.1958	3.1543	24.0415	3.8
1.05	0.9525	0.06533	62.2	27.7080	3.8965	23.8115	4.8
1.25	0.8000	0.07167	57.3	28.2435	4.6287	23.6048	5.6
1.45	0.6897	0.07628	52.6	28.7626	5.3809	23.3817	6.5

TABLE 31.—*Mixture of Calcium Nitrate and Magnesium Nitrate—Data for Freezing-point and Conductivity Measurements, Weight-normal Corrections, and Hydrates.*

<i>m</i>	Fr.-pt.		Weight-normal corrections.					
	$\Delta$	$W_{sol}$	$W_{salt}$	$W_{H_2O}$	Correction, per cent.			
0.5 Ca(NO <sub>3</sub> ) <sub>2</sub> +0.5 Mg(NO <sub>3</sub> ) <sub>2</sub> ....	2.498	26.4387	1.9537	24.4850	2.1			
0.9 Ca(NO <sub>3</sub> ) <sub>2</sub> +0.9 Mg(NO <sub>3</sub> ) <sub>2</sub> ....	4.856	27.5300	3.5166	24.0134	3.9			
1.3 Ca(NO <sub>3</sub> ) <sub>2</sub> +1.3 Mg(NO <sub>3</sub> ) <sub>2</sub> ....	7.624	28.5974	5.0796	23.5178	5.9			
1.7 Ca(NO <sub>3</sub> ) <sub>2</sub> +1.7 Mg(NO <sub>3</sub> ) <sub>2</sub> ....	10.93	29.6600	6.6425	23.0175	7.9			
2.1 Ca(NO <sub>3</sub> ) <sub>2</sub> +2.1 Mg(NO <sub>3</sub> ) <sub>2</sub> ....	14.90	30.6253	8.2055	22.4198	10.3			
2.5 Ca(NO <sub>3</sub> ) <sub>2</sub> +2.5 Mg(NO <sub>3</sub> ) <sub>2</sub> ....	19.73	31.6538	9.7684	21.8854	12.5			
2.9 Ca(NO <sub>3</sub> ) <sub>2</sub> +2.9 Mg(NO <sub>3</sub> ) <sub>2</sub> ....	24.8	32.6175	11.3313	21.2862	14.9			
Conductivity.								
<i>m</i>	<i>m<sub>c</sub></i>	<i>V<sub>c</sub></i>	<i>k<sub>u</sub></i>	<i>k</i>	<i>D</i>	<i>k<sub>c</sub></i>	<i>μ<sub>s</sub></i>	<i>a</i>
0.5 Ca(NO <sub>3</sub> ) <sub>2</sub> ....	0.25	4.0000	0.03683	0.02079	0.00370	0.01901	76.1	0.565
0.5 Mg(NO <sub>3</sub> ) <sub>2</sub> ....	0.25	4.0000		0.02156		0.01982	79.3	0.671
0.9 Ca(NO <sub>3</sub> ) <sub>2</sub> ....	0.45	2.2222	0.05470	0.03326	0.01368	0.02592	57.6	0.428
0.9 Mg(NO <sub>3</sub> ) <sub>2</sub> ....	0.45	2.2222		0.03512		0.02878	64.0	0.498
1.3 Ca(NO <sub>3</sub> ) <sub>2</sub> ....	0.65	1.538	0.06597	0.04293	0.02390	0.02990	46.0	0.342
1.3 Mg(NO <sub>3</sub> ) <sub>2</sub> ....	0.65	1.538		0.04694		0.03607	55.5	0.432
1.7 Ca(NO <sub>3</sub> ) <sub>2</sub> ....	0.85	1.1765	0.07120	0.05027	0.03589	0.03042	35.8	0.266
1.7 Mg(NO <sub>3</sub> ) <sub>2</sub> ....	0.85	1.1765		0.05682		0.04078	48.0	0.373
2.1 Ca(NO <sub>3</sub> ) <sub>2</sub> ....	1.05	0.9523	0.07167	0.05630	0.04996	0.02833	27.0	0.201
2.1 Mg(NO <sub>3</sub> ) <sub>2</sub> ....	1.05	0.9523		0.06533		0.04334	41.3	0.321
2.5 Ca(NO <sub>3</sub> ) <sub>2</sub> ....	1.25	0.8000	0.06914	0.06036	0.06289	0.02481	19.9	0.148
2.5 Mg(NO <sub>3</sub> ) <sub>2</sub> ....	1.25	0.8000		0.07167		0.04443	35.5	0.276
2.9 Ca(NO <sub>3</sub> ) <sub>2</sub> ....	1.45	0.68966	0.06333	0.06323	0.07619	0.01987	13.7	0.102
2.9 Mg(NO <sub>3</sub> ) <sub>2</sub> ....	1.45	0.68966		0.07628		0.04346	30.0	0.233
Hydrates.								
<i>m</i>	<i>L<sub>c</sub></i>		<i>M</i>	Sp gr. cor.	<i>H<sub>c</sub></i>	<i>M<sub>c</sub></i>		
0.5 Ca(NO <sub>3</sub> ) <sub>2</sub> .....	3.96		6.3	2.1	4.6	18.5		
0.5 Mg(NO <sub>3</sub> ) <sub>2</sub> .....	4.16		6.7		5.2	20.8		
0.9 Ca(NO <sub>3</sub> ) <sub>2</sub> .....	3.45		8.0	3.9	7.2	16.0		
0.9 Mg(NO <sub>3</sub> ) <sub>2</sub> .....	3.71		11.7		11.1	24.7		
1.3 Ca(NO <sub>3</sub> ) <sub>2</sub> .....	3.13		10.5	5.9	9.4	14.4		
1.3 Mg(NO <sub>3</sub> ) <sub>2</sub> .....	3.47		15.6		14.9	22.9		
1.7 Ca(NO <sub>3</sub> ) <sub>2</sub> .....	2.85		13.1	7.9	11.7	13.8		
1.7 Mg(NO <sub>3</sub> ) <sub>2</sub> .....	3.25		19.1		18.1	21.3		
2.1 Ca(NO <sub>3</sub> ) <sub>2</sub> .....	2.61		15.7	10.3	13.6	13.0		
2.1 Mg(NO <sub>3</sub> ) <sub>2</sub> .....	3.05		22.4		21.0	20.0		
2.5 Ca(NO <sub>3</sub> ) <sub>2</sub> .....	2.41		18.4	12.5	15.7	12.5		
2.5 Mg(NO <sub>3</sub> ) <sub>2</sub> .....	2.89		25.3		23.3	18.7		
2.9 Ca(NO <sub>3</sub> ) <sub>2</sub> .....	2.24		20.4	14.9	16.5	11.4		
2.9 Mg(NO <sub>3</sub> ) <sub>2</sub> .....	2.73		28.1		25.2	17.4		

The curves in figs. 14 and 15 show the same general relations as the preceding curves of the same character, except those of lithium bromide and sodium bromide. The amount of water eliminated to form hydrates in the mixture tends to diminish somewhat, proportionally to the diminution in the amount of water present which is acting as solvent. This is clearly shown by the direction in which the curves turn with increased concentration of the solutions. It is probable that in the more dilute solu-

TABLE 32.—Hydrating Power in Separate Solutions of Magnesium Nitrate and of Calcium Nitrate.

<i>m</i>	Calcium nitrate in mixtures of calcium nitrate and mag- nesium nitrate.		Magnesium nitrate.	
	$DH_2O$	$D_m$	$DH_2O$	$D_m$
0.25	104.4	1.7	93.7	1.5
0.45	220.3	0.8	150.5	0.6
0.65	298.5	1.1	202.0	0.7
0.85	365.7	1.4	251.0	1.0
1.05	432.5	2.1	300	1.4
1.25	487.0	2.7	351	2.0
1.45	534.0	3.9	381	2.9

FIG. 14.

- I. Difference between Amount of Water Present as Solvent in Single Solution of Calcium Nitrate and in Mixture of Calcium Nitrate and Magnesium Nitrate.
- II. Difference between Values of  $M$  for Calcium Nitrate in Single Solution and in Mixture of Calcium Nitrate and Magnesium Nitrate.

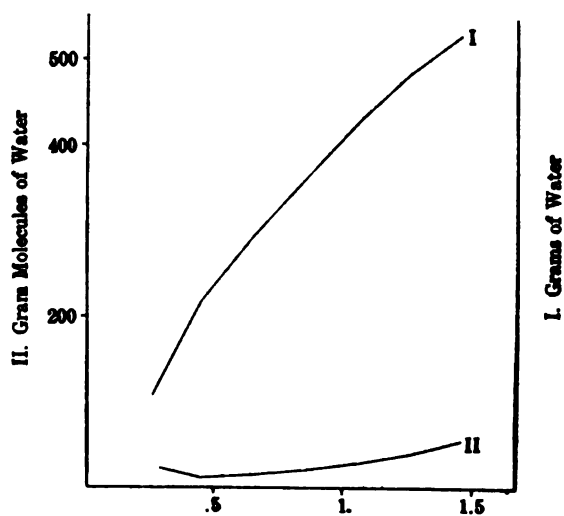
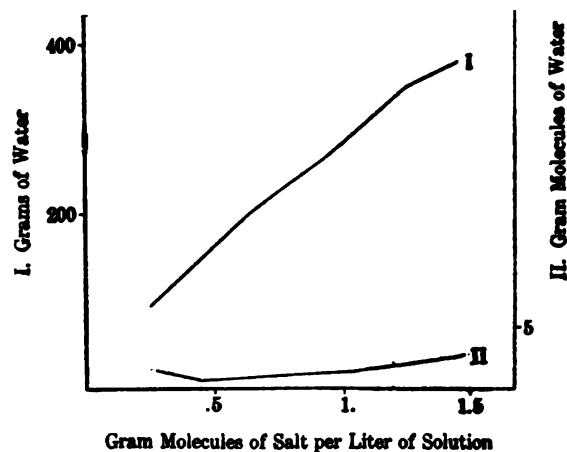


FIG. 15.

- I. Difference between Amount of Water Present as Solvent in Single Solution of Magnesium Nitrate and in Mixture of Magnesium Nitrate and Calcium Nitrate.
- II. Difference between Values of  $M$  for Magnesium Nitrate in Single Solution and in Mixture of Calcium Nitrate and Magnesium Nitrate.



tions we have the difference in the hydrating power of the ions and molecules affecting the total amount of water eliminated as water of hydration. Consequently, where the total amount of salt is constant, but a change in the dissociation is produced, if the number of ions is large relative to the number of molecules undissociated, as is the case in the more dilute solutions, the curve for  $D_m$  does not at once show the influence of diminishing the amount of solvent present. This phenomenon is brought out by the curves as change of direction, or as increased curvature in the curve which represents the value of  $D_m$ .

#### FERRIC CHLORIDE AND ALUMINIUM CHLORIDE.

*A pair of quaternary electrolytes was next studied.* Ferric chloride and aluminium chloride were employed. Very concentrated mother-solutions were prepared, and the necessary measurements were made as quickly as possible, in order to reduce hydrolysis to a minimum, there being an appreciable time factor in the hydrolysis of such compounds as ferric chloride. Notwithstanding all precautions there was, of course, considerable hydrolysis. Especially was this the case in the mixture of the two salts, the presence of the aluminium chloride appearing to act catalytically upon the solution of ferric chloride, causing a gradual precipitation of ferric hydroxide.

It was necessary to extrapolate the value  $84.6^\circ$ , since the solution failed to freeze in the freezing mixture employed, *i. e.*, solid carbon dioxide and alcohol. The more concentrated solutions became so viscous when cooled down that it was difficult to stir them properly.

TABLE 33.—*Aluminium Chloride—Data for Freezing-point and Conductivity Measurements, Weight-normal Corrections, and Hydrates.*

$m$	Freezing-point.		Hydrates.				
	$\Delta$	$\Delta/m$	$a$	$L$	$L'$	$M$	$H$
0.2	1.279	6.40	0.660	5.54	6.39	7.4	37.0
0.4	2.910	7.28	0.558	4.97	7.23	7.4	43.5
0.6	5.144	8.57	0.487	4.58	8.47	25.5	42.5
0.8	7.962	9.95	0.421	4.21	9.77	31.6	39.5
1.0	11.795	11.80	0.367	3.91	11.52	36.7	36.7
1.2	16.385	13.65	0.314	3.61	13.25	40.4	33.7
1.3617	21.75	15.97	0.273	3.39	15.44	43.4	31.9
1.415	23.50	16.60					

$m$	Conductivity.			Weight-normal corrections.			
	$V$	$k$	$\mu_0$	$W_{\text{sol}}$	$W_{\text{sol}}$	$W_{H_2O}$	Correction, per cent.
0.2	5.000	0.02398	119.9	25.6240	0.6673	24.9567	0.2
0.4	2.500	0.04053	101.3	26.1538	1.3346	24.8192	0.7
0.6	1.6666	0.05311	88.5	26.7134	2.0019	24.7115	1.2
0.8	1.250	0.06118	76.5	27.2153	2.6692	24.5461	1.8
1.0	1.000	0.06659	66.6	27.7351	3.3365	24.3986	2.4
1.2	0.8333	0.06842	57.0	28.2877	4.0038	24.2839	2.9
1.3617	0.7344	0.06760	49.7	28.7252	4.5433	24.1819	3.3

TABLE 34.—*Ferric Chloride—Data for Freezing-point and Conductivity Measurements, Weight-normal Corrections, and Hydrates.*

<i>m</i>	Freezing-point.		Hydrates.				
	$\Delta$	$\Delta/m$	$\alpha$	<i>L</i>	<i>L'</i>	<i>M</i>	<i>H</i>
0.2	1.255	6.28	0.541	4.88	6.25	12.2	61.0
0.4	2.715	6.79	0.430	4.26	6.72	20.3	50.7
0.6	4.530	7.55	0.352	3.82	7.41	26.9	44.8
0.8	6.667	8.33	0.292	3.49	8.12	31.7	39.6
1.0	9.152	9.15	0.241	3.21	8.85	35.4	35.4
1.2	12.11	10.09	0.201	2.98	9.70	38.5	32.1
1.3617	14.592	10.72	0.173	2.82	10.23	40.2	29.5

<i>m</i>	Conductivity.			Weight-normal corrections.			
	<i>V</i>	<i>k</i>	$\mu_v$	<i>W</i> <sub>sol</sub>	<i>W</i> <sub>salt</sub>	<i>W</i> <sub>H<sub>2</sub>O</sub>	Correction, per cent.
0.2	5.000	0.02380	119.0	25.6792	0.8113	24.8679	0.5
0.4	2.500	0.03786	94.7	26.3380	1.6225	24.7155	1.1
0.6	1.6666	0.04645	77.4	26.9956	2.4337	24.5619	1.8
0.8	1.250	0.05147	64.3	27.6230	3.2450	24.3780	2.5
1.0	1.000	0.05315	53.1	28.2400	4.056	24.1840	3.3
1.2	0.8333	0.05314	44.3	28.8867	4.8675	24.0192	3.9
1.3617	0.7344	0.05178	38.0	29.3690	5.5234	23.8456	4.6

TABLE 35.—*Mixture of Ferric Chloride and Aluminium Chloride—Data for Freezing-point and Conductivity Measurements, Weight-normal Corrections, and Hydrates.*

<i>m</i>	Fr.-pt.		Weight-normal corrections.			
	$\Delta$		<i>W</i> <sub>sol</sub>	<i>W</i> <sub>salt</sub>	<i>W</i> <sub>H<sub>2</sub>O</sub>	Correction, per cent.
0.4 FeCl <sub>3</sub> +0.4 AlCl <sub>3</sub> .....	2.938		26.2807	1.4786	24.8021	0.8
0.8 FeCl <sub>3</sub> +0.8 AlCl <sub>3</sub> .....	7.28		27.4365	2.9571	24.4794	2.1
1.2 FeCl <sub>3</sub> +1.2 AlCl <sub>3</sub> .....	13.69		28.5660	4.4356	24.1304	3.5
1.6 FeCl <sub>3</sub> +1.6 AlCl <sub>3</sub> .....	22.5		29.7105	5.9142	23.7963	4.8
2.0 FeCl <sub>3</sub> +2.0 AlCl <sub>3</sub> .....	36.0		30.8182	7.3925	23.4257	6.3
2.4 FeCl <sub>3</sub> +2.4 AlCl <sub>3</sub> .....	56.0		31.9182	8.8713	23.0469	7.8
2.7234 FeCl <sub>3</sub> +2.7234 AlCl <sub>3</sub> .....	84.6		32.7777	10.0667	22.7110	9.2

Conductivity measurements.								
<i>m</i>	<i>m</i> <sub>c</sub>	<i>V</i> <sub>c</sub>	<i>k</i> <sub>n</sub>	<i>k</i>	<i>D</i>	<i>k</i> <sub>c</sub>	$\mu_v$	$\alpha$
0.4 FeCl <sub>3</sub> ....	0.2	5.000	0.04032	0.02380	0.00746	0.01935	96.8	0.440
0.4 AlCl <sub>3</sub> ....	0.2	5.000		0.02398		0.02097	104.8	0.577
0.8 FeCl <sub>3</sub> ....	0.4	2.500	0.06046	0.03786	0.01793	0.02662	67.3	0.306
0.8 AlCl <sub>3</sub> ....	0.4	2.500		0.04053		0.03353	83.7	0.461
1.2 FeCl <sub>3</sub> ....	0.6	1.6666	0.05587	0.04645	0.04369	0.01906	31.8	0.144
1.2 AlCl <sub>3</sub> ....	0.6	1.6666		0.05311		0.03681	61.4	0.338
1.6 FeCl <sub>3</sub> ....	0.8	1.250	0.05690	0.05147	0.05575	0.01604	20.1	0.091
1.6 AlCl <sub>3</sub> ....	0.8	1.250		0.06118		0.04066	51.1	0.281
2.0 FeCl <sub>3</sub> ....	1.0	1.00	0.04792	0.05315	0.07183	0.00660	6.6	0.030
2.0 AlCl <sub>3</sub> ....	1.0	1.00		0.06659		0.04132	41.3	0.227
2.4 FeCl <sub>3</sub> ....	1.2	0.8333	0.03787	0.05314	0.08370	0.00000	00.0	0.000
2.4 AlCl <sub>3</sub> ....	1.2	0.8333		0.06842		0.03787	31.6	0.174
2.72 FeCl <sub>3</sub> ....	1.3617	0.7344	0.02959	0.05178	0.08978	0.00000	00.0	0.000
2.72 AlCl <sub>3</sub> ....	1.3617	0.7344		0.06760		0.02959	21.7	0.120

TABLE 35—Continued.

<i>m</i>	Hydrates.				
	<i>L<sub>c</sub></i>	<i>M</i>	Sp. gr. cor.	<i>M<sub>c</sub></i>	<i>H<sub>c</sub></i>
0.4 FeCl <sub>3</sub> .....	4.31	12.2	0.8	13.5	67.5
0.4 AlCl <sub>3</sub> .....	5.08	7.4		8.2	41.0
0.8 FeCl <sub>3</sub> .....	3.57	20.3	2.1	19.6	49.0
0.8 AlCl <sub>3</sub> .....	4.44	17.4		16.6	41.5
1.2 FeCl <sub>3</sub> .....	2.67	26.9	3.5	25.8	43.0
1.2 AlCl <sub>3</sub> .....	3.74	25.5		24.4	40.7
1.6 FeCl <sub>3</sub> .....	2.37	31.7	4.8	29.0	36.2
1.6 AlCl <sub>3</sub> .....	3.43	31.6		28.9	36.1
2.0 FeCl <sub>3</sub> .....	2.03	35.4	6.3	32.2	32.2
2.0 AlCl <sub>3</sub> .....	3.02	36.7		33.7	33.7
2.4 FeCl <sub>3</sub> .....	1.86	38.5	7.8	34.6	28.8
2.4 AlCl <sub>3</sub> .....	2.83	40.4		36.7	30.6
2.7234 FeCl <sub>3</sub> .....	1.86	40.2	9.2	36.1	26.5
2.7234 AlCl <sub>3</sub> .....	2.53	43.4		39.6	29.0

It is to be noted that the conductivity measurements which are given in table 35 are the merest approximations to measurements of dissociation. The conductivity measurements are made at zero, whereas some of these mixtures freeze very considerably below 0°C. There is marked hydrolysis in some cases, as already mentioned, leading to a precipitation of the iron. There is considerable difference between the viscosity of the single solutions and of the mixtures where the normalities are the same. The assumption that these salts dissociate at once, in the most concentrated solutions, into  $M^{+++} + 3Cl^{-}$ , is certainly not correct. Finally, the values of  $\mu_{\infty}$  are obtained by calculation, and may differ considerably from the true values because of the factors just mentioned.

The values of  $M$  and of  $M_c$  are plotted as curves in fig. 16. The general relation shown by these curves are the same as have previously been pointed out. The fact that the hydrating power of both the aluminium chloride and the ferric chloride is apparently greater in the mixture than in the separate solutions, in the most dilute solutions employed, is probably due to the effect of hydrolysis in increasing the value of  $L$ , and consequently diminishing  $M$ , though it may possibly be due, in part, to change in dissociation and difference in the hydrating power of the ions and molecules. It

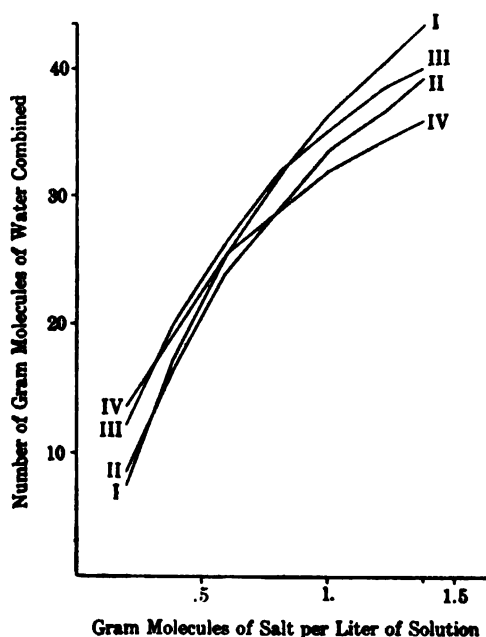


FIG. 16.

- I. Aluminium Chloride Alone.
- II. Aluminium Chloride Mixed with Ferric Chloride.
- III. Ferric Chloride Alone.
- IV. Ferric Chloride Mixed with Aluminium Chloride.

should be noted, also, that the hydrating power of the aluminium chloride appears to be relatively less than that of the ferric chloride in the more dilute solutions, but that this relation is reversed in the more concentrated solutions. This may be due to hydrolysis, since, if the aluminium chloride hydrolyzes more rapidly than the ferric chloride, then, in the more dilute solutions, where the effects of hydrolysis would be pronounced, the result would be to increase the value of  $L$  and, consequently, to diminish the value of  $M$ , based upon it.

In table 36 the abbreviations have the usual significance. The values are plotted as curves in figs. 17 and 18.

TABLE 36.—*Aluminium Chloride and Ferric Chloride.*

$m$	Aluminium chloride in mixture of aluminium chloride and ferric chloride.		Ferric chloride in mixture of aluminium chloride and ferric chloride.	
	$DH_2O$	$D_m$	$DH_2O$	$D_m$
0.2	367	-0.8	150	-1.3
0.4	249	0.8	308	0.7
0.6	488	1.1	456	1.1
0.8	552	2.7	543	2.7
1.0	618	3.0	636	3.2
1.2	671	3.7	699	3.9
1.3617	709	3.8	758	4.1

FIG. 17.

I. Difference between the Amount of Water Present as Solvent in the Single Solution of Aluminium Chloride and in the Mixture of Ferric Chloride and Aluminium Chloride.

II. Difference between the Values of  $M$  for Aluminium Chloride in Single Solution and in the Mixture of Aluminium Chloride and Ferric Chloride.

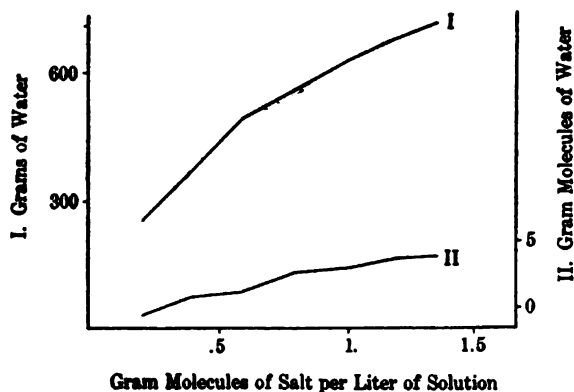
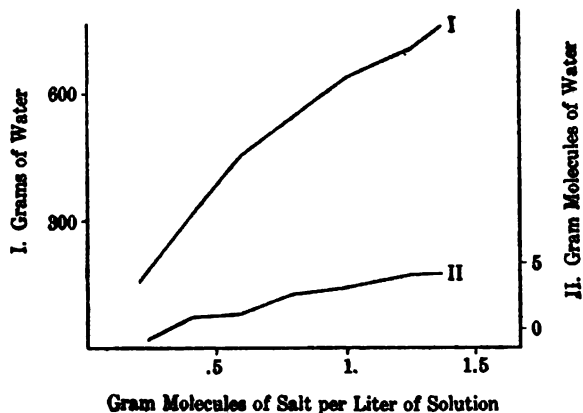


FIG. 18.

I. Difference between Amount of Water Present as Solvent in the Single Solution of Ferric Chloride and in the Mixture of Ferric Chloride and Aluminium Chloride.

II. Difference between Values of  $M$  for Ferric Chloride in Single Solution and in the Mixture of Ferric Chloride and Aluminium Chloride.



The effect of decrease in the amount of water present as solvent is plainly shown in the diminishing values of  $M$  as the amount of solvent is lessened. The slight irregularities are probably due to unavoidable experimental error, and inaccuracy of the conductivity method as a measure of dissociation.

#### CALCIUM NITRATE AND CALCIUM CHLORIDE.

Thus far all of the salts studied have a common anion. In order to extend the investigation to a pair of salts having a common cation, a mixture of calcium nitrate and calcium chloride was employed. The data for separate solutions of these two salts have been given. The results obtained with the mixture are shown in table 37.

TABLE 37.—*Mixture of Calcium Nitrate and Calcium Chloride—Data for Freezing-point and Conductivity Measurements, Weight-normal Corrections, and Hydrates.*

$m$	Fr.-pt.	Weight-normal corrections.			
	$\Delta$	$W_{sol}$	$W_{salt}$	$WH_2O$	Correction, per cent.
0.5 Ca(NO <sub>3</sub> ) <sub>2</sub> +0.5 CaCl <sub>2</sub> .....	2.50	26.3336	1.7197	24.6139	1.5
0.9 Ca(NO <sub>3</sub> ) <sub>2</sub> +0.9 CaCl <sub>2</sub> .....	4.88	27.3415	3.0954	24.2461	3.0
1.3 Ca(NO <sub>3</sub> ) <sub>2</sub> +1.3 CaCl <sub>2</sub> .....	7.67	28.3615	4.4711	23.8904	4.4
1.7 Ca(NO <sub>3</sub> ) <sub>2</sub> +1.7 CaCl <sub>2</sub> .....	11.00	29.3082	5.8469	23.4613	6.2
2.1 Ca(NO <sub>3</sub> ) <sub>2</sub> +2.1 CaCl <sub>2</sub> .....	14.78	30.2933	7.3260	23.0707	7.7
2.5 Ca(NO <sub>3</sub> ) <sub>2</sub> +2.5 CaCl <sub>2</sub> .....	19.20	31.2197	8.5984	22.6213	9.5
2.9 Ca(NO <sub>3</sub> ) <sub>2</sub> +2.9 CaCl <sub>2</sub> .....	24.2	32.1762	9.9741	22.2021	11.2
3.311 Ca(NO <sub>3</sub> ) <sub>2</sub> +3.311 CaCl <sub>2</sub> ....	30.7	33.0792	11.3878	21.6914	13.2

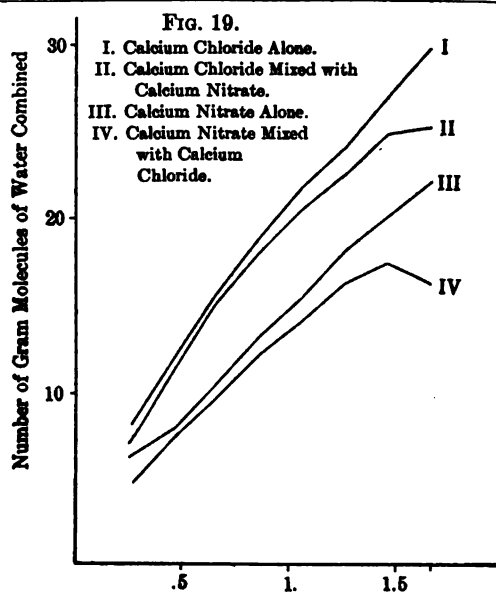
Conductivity measurements.								
$m$	$m_c$	$V_c$	$k_u$	$k$	$D$	$k_c$	$\mu_s$	$a$
0.5 Ca(NO <sub>3</sub> ) <sub>2</sub> ....	0.25	4.0000	0.03947	0.02097	0.05573	0.01825	73.0	0.543
0.5 CaCl <sub>2</sub> .....	0.25	4.0000		0.02407		0.02122	84.9	0.575
0.9 Ca(NO <sub>3</sub> ) <sub>2</sub> ....	0.45	2.2222	0.05994	0.03259	0.01301	0.02678	59.5	0.442
0.9 CaCl <sub>2</sub> .....	0.45	2.2222		0.03964		0.03316	73.7	0.499
1.3 Ca(NO <sub>3</sub> ) <sub>2</sub> ....	0.65	1.5380	0.07355	0.04263	0.02362	0.03083	47.4	0.353
1.3 CaCl <sub>2</sub> .....	0.65	1.5380		0.05424		0.04272	65.7	0.455
1.7 Ca(NO <sub>3</sub> ) <sub>2</sub> ....	0.85	1.1765	0.08180	0.05027	0.03538	0.03169	37.3	0.277
1.7 CaCl <sub>2</sub> .....	0.85	1.1765		0.06690		0.05011	59.0	0.400
2.1 Ca(NO <sub>3</sub> ) <sub>2</sub> ....	1.05	0.9523	0.08410	0.05630	0.05044	0.02927	27.9	0.207
2.1 CaCl <sub>2</sub> .....	1.05	0.9523		0.07834		0.05483	52.2	0.354
2.5 Ca(NO <sub>3</sub> ) <sub>2</sub> ....	1.25	0.8000	0.06828	0.06036	0.06653	0.02375	19.0	0.141
2.5 CaCl <sub>2</sub> .....	1.25	0.8000		0.08885		0.05893	47.1	0.320
2.9 Ca(NO <sub>3</sub> ) <sub>2</sub> ....	1.45	0.68966	0.07715	0.06324	0.08347	0.01637	11.3	0.084
2.9 CaCl <sub>2</sub> .....	1.45	0.68966		0.09738		0.06078	41.9	0.284
3.311 Ca(NO <sub>3</sub> ) <sub>2</sub> ....	1.6555	0.60405	0.06985	0.06467	0.09812	0.00865	5.2	0.039
3.311 CaCl <sub>2</sub> .....	1.6555	0.60405		0.00330		0.06120	37.0	0.251

TABLE 37—Continued.

Hydrates.					
<i>m</i>	<i>L<sub>c</sub></i>	<i>M</i>	Sp. gr. cor.	<i>M<sub>c</sub></i>	<i>H<sub>c</sub></i>
0.5 Ca(NO <sub>3</sub> ) <sub>2</sub> .....	3.88	6.3	1.5	4.6	18.4
0.5 CaCl <sub>2</sub> .....	4.00	8.2		7.0	28.0
0.9 Ca(NO <sub>3</sub> ) <sub>2</sub> .....	3.51	8.0	3.0	7.4	16.4
0.9 CaCl <sub>2</sub> .....	3.72	11.7		11.2	24.9
1.3 Ca(NO <sub>3</sub> ) <sub>2</sub> .....	3.17	10.5	4.4	9.5	14.8
1.3 CaCl <sub>2</sub> .....	3.52	15.7		15.1	23.2
1.7 Ca(NO <sub>3</sub> ) <sub>2</sub> .....	2.89	13.1	6.2	12.1	14.2
1.7 CaCl <sub>2</sub> .....	3.35	18.9		18.2	21.4
2.1 Ca(NO <sub>3</sub> ) <sub>2</sub> .....	2.63	15.7	7.7	14.1	13.4
2.1 CaCl <sub>2</sub> .....	3.18	21.9		20.8	19.8
2.5 Ca(NO <sub>3</sub> ) <sub>2</sub> .....	2.39	18.4	9.5	16.4	13.1
2.5 CaCl <sub>2</sub> .....	3.05	24.3		22.8	18.2
2.9 Ca(NO <sub>3</sub> ) <sub>2</sub> .....	2.17	20.4	11.2	17.6	12.1
2.9 CaCl <sub>2</sub> .....	2.92	27.3		25.2	17.4
3.311 Ca(NO <sub>3</sub> ) <sub>2</sub> .....	2.01	22.4	13.2	16.4	9.9
3.311 CaCl <sub>2</sub> .....	2.79	30.1		25.6	15.5

The values of *M* shown in table 37 are plotted as curves in fig. 19. The results are of the same character as those shown by the preceding mixtures. The most concentrated solution measured shows a somewhat lower value for *M* in the mixture than we should expect, but it must be borne in mind that at this great concentration the experimental errors involved are necessarily very large.

Table 38 contains the data necessary to compare the change in the amount of solvent present with the change in the values of *M* in separate solution and in the mixture.



Gram Molecules of Salt per Liter of Solution

TABLE 38.—Hydrating Power in Solutions of Calcium Nitrate and Calcium Chloride.

<i>m</i>	Calcium chloride in mixture of calcium nitrate and calcium chloride.		Calcium nitrate in mixture of calcium nitrate and calcium chloride.	
	<i>DH<sub>2</sub>O</i>	<i>D<sub>m</sub></i>	<i>DH<sub>2</sub>O</i>	<i>D<sub>m</sub></i>
0.25	92	1.2	131	1.7
0.45	153	0.5	213	0.6
0.65	202	0.6	288	0.9
0.85	260	0.7	350	1.0
1.05	306	1.1	404	1.6
1.25	358	1.5	447	2.0
1.45	392	2.1	496	2.8
0.65	386	4.5	575	6.0

The values are plotted as curves in figs. 20 and 21. A diminution in the amount of water present as solvent causes a diminution in the value of  $M$ . This effect appears to be greater with increasing concentration. It is probable that in the most dilute solutions the difference in the hydrating power of the ions and molecules affects the curve, changing its direction.

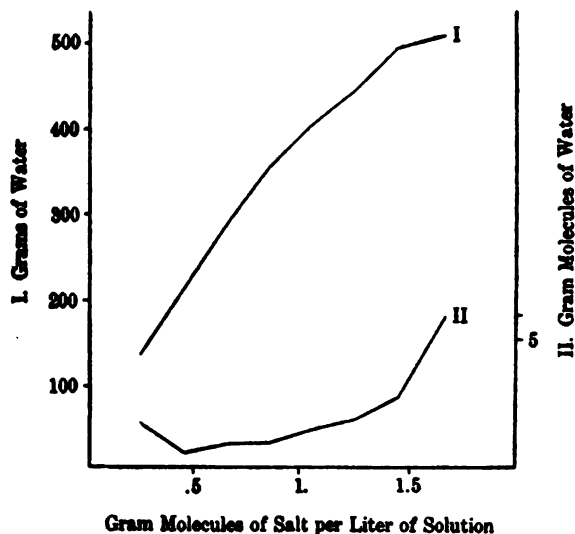


FIG. 20.

- I. Difference between the Amount of Water acting as Solvent toward the Calcium Nitrate in the Mixture of Calcium Nitrate and Calcium Chloride, and in the Separate Solution of Calcium Nitrate.
- II. Difference between the Values of  $M$  for Calcium Nitrate in Separate Solution and in the Mixture of Calcium Nitrate and Calcium Chloride.

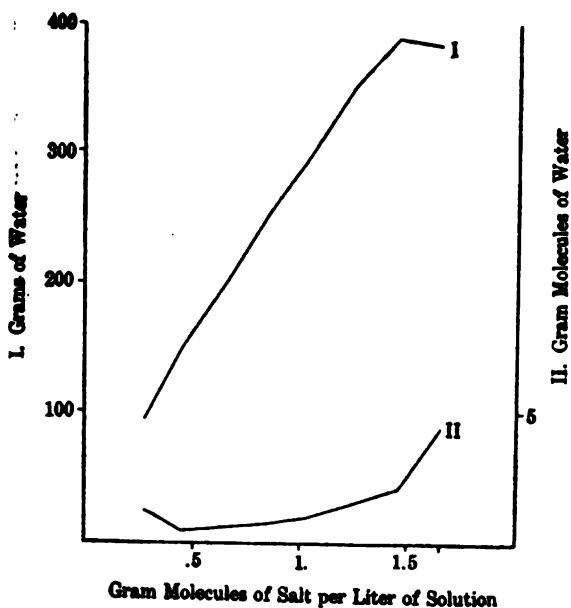


FIG. 21.

- I. Difference between the Amount of Water acting as Solvent toward the Calcium Chloride in the Mixture of Calcium Nitrate and Calcium Chloride and in the Separate Solution of Calcium Chloride.
- II. Difference between the Values of  $M$  for Calcium Chloride in Separate Solution and in the Mixture of Calcium Nitrate and Calcium Chloride.

## EFFECT OF CHANGE IN TEMPERATURE ON THE CONDUCTIVITIES OF SEPARATE SOLUTIONS OF ELECTROLYTES AND ON MIXTURES OF THESE ELECTROLYTES.

In this work we have repeatedly called attention to the fact that the conductivity method furnishes us with only an approximate value of the dissociation of a salt. The conductivity method of measuring dissociation is, however, the most general one available. In order to study the effect of change of temperature on the conductivities of separate solutions of electrolytes, and upon mixtures of these electrolytes, it was necessary to select a pair of salts which do not form double salts in solution, and which have little or no hydrating power. Potassium chloride and ammonium chloride were used.

The conductivities of single solutions of these salts and of their mixture were studied at 0° and 12° C. Comparisons having shown that our values agree very closely with those obtained by Jones and West<sup>1</sup> and by Jones and Knight,<sup>2</sup> the values of Jones and Knight, at 25° C., were used. The values of Jones and West, at 18° C., show a very close agreement with those obtained experimentally by Kohlrausch at the same temperature. The values for potassium chloride at 25° C. are taken from the results of Kohlrausch.

Since we are employing some of the values of Jones and West, Jones and Knight, and Kohlrausch, at 25° C., we have tabulated a few values taken from these sources side by side with our own (tables 39, 40, and 41).

TABLE 39.—Molecular Conductivities of Potassium Chloride and Ammonium Chloride.

V	Potassium chloride.				Ammonium chloride.			
	$\mu, 0^\circ$	$\mu, 12^\circ$	V	$\mu, 25^\circ$	$\mu, 0^\circ$	$\mu, 12^\circ$	V	$\mu, 25^\circ$
1	61.58	82.05	1	104.1	61.08	81.15	1	99.3
2	63.02	84.43	2	108.6	62.53	83.57	2	104.9
5	65.85	87.84	4	111.2	63.98	87.66	4	110.4
20	68.59	92.88	16	121.5	68.13	93.19	16	120.9
100	72.13	98.69	80	128.5	71.64	99.94	80	131.8
200	73.73	101.3	160	131.1	72.89	101.3	160	134.2
1000	74.31	103.3	640	133.9	74.10	103.7	640	138.1

TABLE 40.—Comparison of Conductivities—Potassium Chloride.

V	Jones and Stine. $\mu, 0^\circ$	Jones and West. $\mu, 0^\circ$	Jones and West. $\mu, 18^\circ$	Kohlrausch. $\mu, 18^\circ$	V	Jones and West. $\mu, 25^\circ$	Jones and Knight. (Kohlrausch.) $\mu, 25^\circ$
1	61.58				1		104.5
2	63.02	62.96	95.9	95.8	2	109.5	108.6
5	65.85				8	118.6	116.5
8		66.47	103.6		16	122.9	121.5
16		68.40	107.0		32	126.8	125.4
20	68.59			108.3	128	132.4	
32		70.27	110.7		160		131.1
120	72.13			114.7	512	135.5	
128		73.00	115.5		640		133.9
200	73.73				1024	137.0	
1000	74.31			119.3	1600		135.4
1024		75.14	119.3				

<sup>1</sup>Amer. Chem. Journ., 34, 381 (1905).<sup>2</sup>Ibid., 22, 125 (1899).

TABLE 41.—Comparison of Conductivities—Ammonium Chloride.

<i>V</i>	Jones and Stine. $\mu, 0^\circ$	Jones and West. $\mu, 0^\circ$	Jones and West. $\mu, 18^\circ$	Kohl- rausch. $\mu, 18^\circ$	<i>V</i>	Jones and West. $\mu, 25^\circ$	Jones and West. $\mu, 25^\circ$	<i>V</i>	Jones and Knight. $\mu, 25^\circ$	Jones and Knight. $\mu, 25^\circ$
1	61.08	.....	.....	.....	1	.....	99.3	160	.....	134.2
2	62.53	62.76	96.3	94.8	2	109.2	104.9	512	136.8	.....
5	63.98	.....	.....	.....	8	118.6	115.8	640	.....	138.1
8	.....	66.17	103.6	.....	16	123.2	120.9	1024	137.8	.....
16	.....	68.02	107.2	.....	32	127.6	125.3	1600	.....	138.9
20	68.13	.....	.....	107.8	128	133.4	.....	.....	.....	.....
32	.....	70.2	110.8	.....						
100	71.64	.....	.....	114.2						
128	.....	73.08	.....	.....						
200	72.89	.....	116.2	.....						
1000	74.10	.....	.....	119.0						
1024	.....	74.84	119.6	.....						

In connection with the conductivity of ammonium chloride, Jones and Knight say:<sup>1</sup>

The value which we found for the conductivity of ammonium chloride differed slightly from those obtained by Kohlrausch,<sup>2</sup> our values being somewhat lower in the more concentrated solutions, and a little higher in the more dilute. This difference is probably due to the temperature coefficient which must be added to Kohlrausch's values to transform them from  $18^\circ$  to  $25^\circ$ .

This coefficient was uncertain over any considerable range of temperature. It is evident that our values agree very well with those of Kohlrausch, Jones and West, and Jones and Knight.

Let us turn, now, to the conductivities of the mixtures of potassium chloride and ammonium chloride. These solutions were mixed in equal volumes. When, for example, a 2.0 N solution of potassium chloride is added to an equal volume of 2.0 N ammonium chloride the assumption that the resulting solution consists of 1.0 N potassium chloride and 1.0 N ammonium chloride is not quite correct, because of the volume occupied by the salt in the added solution. To make the necessary correction for this factor, pycnometer measurements were made with the more concentrated solutions. In the more dilute solutions this factor is entirely negligible.

TABLE 42.—Specific Gravity Measurements.

Potassium chloride, at $12^\circ$ .					Ammonium chloride, at $12^\circ$ .				
<i>m</i>	<i>C</i>	<i>W<sub>salt</sub></i>	<i>W<sub>H<sub>2</sub>O</sub></i>	<i>V</i>	<i>m</i>	<i>C</i>	<i>W<sub>salt</sub></i>	<i>W<sub>H<sub>2</sub>O</sub></i>	<i>V</i>
0.05	24.4259	0.0911	24.3821	998.66	0.2	24.3605	0.2608	24.1679	992.54
0.20	23.9474	0.35373	23.8077	994.62	0.4	24.4259	0.5229	24.0573	985.37
0.50	11.6945	0.4362	11.5294	986.35	0.6	23.9474	0.7690	23.4098	978.00
1.00	12.6976	0.9472	12.3370	972.16	0.8	12.6976	0.5437	12.3176	970.52
					1.0	11.6945	0.6259	11.2574	963.07

In table 42, *m* is the normality; *C* is the capacity of the pycnometer in cubic centimeters; *W<sub>salt</sub>* is the weight of salt present in the solution; *W<sub>H<sub>2</sub>O</sub>* is the weight of water present in the volume of solution contained in the pycnometer; and *V* is the volume of water in 1,000 cubic centimeters of the solution.

Based upon these measurements, the conductivity of the potassium chloride and ammonium chloride in the various mixtures was calculated, on the assumption that

<sup>1</sup>Amer. Chem. Jour., 22, 117 (1899).<sup>2</sup>Wied. Amer., 26, 161.

no change in the dissociation of these salts takes place when their solutions are mixed. The results are given, along with the conductivities of the mixtures, in table 43.

TABLE 43.—Potassium Chloride and Ammonium Chloride.

						Jones and Knight.					
V	KCl $\mu$ , 25°	NH <sub>4</sub> Cl $\mu$ , 25°	Sum.	KCl+NH <sub>4</sub> Cl		V	KCl $\mu$ , 12°	NH <sub>4</sub> Cl $\mu$ , 12°	Sum.	KCl+NH <sub>4</sub> Cl	
				$\mu$ , 25°	Diff.					$\mu$ , 12°	Diff.
1	104.1	99.3	203.4	179.3	24.1	1	81.95	81.10	163.1	154.9	8.2
2	108.6	104.9	213.5	195.0	18.5	2	84.38	83.55	167.9	161.1	6.8
4	111.2	110.4	221.6	208.3	13.3	5	87.82	87.66	175.5	170.5	5.0
8	116.5	115.8	232.3	220.9	11.4	20	92.88	93.19	186.1	181.3	4.8
16	121.5	120.9	242.4	231.7	10.7	100	98.69	99.94	198.6	194.7	3.9
32	125.4	125.3	250.7	241.2	9.5	200	101.3	101.3	202.6	199.7	2.9
40	125.7	127.6	253.3	245.9	7.4	1000	103.3	103.7	207.0	208.7	-1.7
80	128.5	131.8	260.3	254.3	6.0						
160	131.1	134.2	265.3	263.3	3.0						
320	132.1	136.8	268.9	267.0	1.9						
640	133.9	138.1	272.0	273.1	-1.1						
1600	135.4	138.9	274.3	279.1	-4.8						

V	KCl $\mu$ , 0°	NH <sub>4</sub> Cl $\mu$ , 0°	Sum.	KCl+NH <sub>4</sub> Cl		Comparison of differences.		
				$\mu$ , 0°	Diff.	Diff. 0°	Diff. 12°	Diff. 25°
1	61.48	61.03	122.5	121.2	1.3	1.3	8.2	24.1
2	62.97	62.51	125.5	122.8	2.7	2.7	6.8	18.5
5	65.83	63.97	129.8	126.9	2.9	2.9	5.0	12.8
20	68.59	68.13	136.7	133.4	3.3	3.3	4.8	10.4
100	72.13	71.64	143.6	141.2	2.6	2.6	3.9	5.2
200	73.73	72.89	146.6	144.9	1.7	1.7	2.9	2.7
1000	74.31	74.10	148.4	147.5	0.9	0.9	-1.7	-2.5

If this change in the conductivity, when the solutions are mixed, is due only to a suppression of ionization, then we should expect the suppression to be nearly the same at the various temperatures, since the dissociation is very nearly the same at these various temperatures (*vide* table 44).

TABLE 44.—Dissociation of Potassium and Ammonium Chlorides.

V	Dissociation of potassium chloride.			Dissociation of ammonium chloride.		
	$\alpha$ 0°	$\alpha$ 12°	$\alpha$ 25°	$\alpha$ 0°	$\alpha$ 12°	$\alpha$ 25°
1	0.827	0.793	0.768	0.824	0.782	0.715
2	0.847	0.817	0.802	0.844	0.806	0.755
5	0.886	0.850	0.831	0.863	0.845	0.805
20	0.923	0.899	0.905	0.919	0.899	0.878
100	0.971	0.955	0.954	0.967	0.964	0.953
200	0.992	0.981	0.970	0.984	0.977	0.970
1000	1.00	1.00	0.993	1.00	1.00	0.997

If the suppression of the ionization is the only cause of the diminution in the conductivity when the solutions are mixed, then the greatest diminution should take place where the more highly dissociated salts are mixed; that is, the diminution in conductivity should be slightly greater at 0° than at 12° C., and slightly greater at 12° C. than at 25° C. Just the opposite is shown to be true by table 43. Again, if this lessening of conductivity is dependent upon the amount of dissociation alone, then, since the difference between the dissociation at 0° and 12° C. is the same or a

little greater than the difference between the dissociation at 12° and 25° C. (except in some cases in the ammonium chloride), we should expect to find the difference between the columns headed Diff. 12° and Diff. 0°, in table 43, the same or slightly greater than the difference between the columns headed Diff. 12° and Diff. 25°. The opposite is true, the difference between columns 2 and 3 being from two to four times as great as that between 1 and 2, up to  $V=100$ . At  $V=100$  the differences are the same, and at  $V=200$  and  $V=1,000$  the column headed Diff. 25° becomes smaller than the other two.

We must, then, look elsewhere for the cause of at least a part of the change in the conductivities, since it is evidently not due *solely* to change in dissociation, especially since some of the solutions mixed are nearly isohydric. There are three other factors which might come into play: change in hydration, giving rise to a change in the dimensions of the ionic sphere; change in the viscosity of the solution with change in temperature; change in the number of the dissolved particles (ions and molecules). Of these three possibilities the first probably does not affect the conductivity appreciably, there being little hydration in these cases. The second is probably the principal factor in causing changes in the conductivity with changes in temperature. The third—change in the number of the dissolved particles—may also play some part, since the value of  $\alpha$  becomes smaller with rise in temperature, and, other things being equal, the fewer the number of ions and molecules with which a moving ion must collide, the less the friction it will encounter. The differences in the values of columns 1, 2, and 3 are greatest for the most concentrated solutions, and it is in these solutions that the greatest change in the value  $\alpha$  with rise in temperature is noted.

Clearly, values for  $\alpha$  which are based upon the conductivity of the completely dissociated molecules at high dilution can not be strictly correct, since the conductivity of this completely dissociated solution must be considerably altered by change in viscosity and in the number of dissolved ions or molecules, both of which factors enter in increasing the concentration, the number of ions and molecules present undergoing especially great alteration.

#### SUMMARY.

It has been shown:

1. That the complexity of the hydrates formed by a salt is a function of the amount of water present as solvent.
2. That when two salts are present in the same solution, the complexity of the hydrates is somewhat less than in separate solutions of these salts, each salt tending to dehydrate the other.
3. That the ions and the molecules of salts probably have different hydrating power.
4. That the hydrating power of the molecules is in some cases probably greater than that of the ions into which these molecules dissociate.
5. Additional proof is furnished for the view that the conductivity method is by no means an accurate measure of dissociation in concentrated solutions.
6. It has been pointed out that the diminution in conductivity which takes place when two electrolytes of the type potassium chloride-ammonium chloride are mixed is probably not due entirely to suppression of ionization, but also to (a) change in the viscosity of the solvent; (b) change in the size of the ionic sphere, due to alteration in the amount of water which the ion must drag with it through the solution.

## WORK OF J. N. PEARCE.

### INTRODUCTION.

The conductivity of a solution of an electrolyte is a function of several conditions: the nature of the electrolyte and the degree of its dissociation, the speed of its component ions, and the viscosity of the solvent. The degree of dissociation, in turn, depends upon the concentration of the electrolyte and the nature of the solvent.

As was pointed out by Dutoit and Aston, that solvent whose molecules are associated to the greatest extent has the greatest dissociating power.

Weak acids, weak bases, and salts of weak acids and bases show constantly increasing dissociation with increasing dilution; but, within the limits of accuracy of our present methods, no maximum of conductivity is directly obtainable. On the other hand, strong electrolytes show rapidly increasing dissociation with slight increase in dilution—a maximum conductivity being reached at moderate dilution.

It is stated by Ostwald<sup>1</sup> that the anions of the halogen acids move more rapidly than do those of the oxyhalogen acids, *e. g.*,  $\text{ClO}_3$ ,  $\text{BrO}_3$ ,  $\text{IO}_3$ ; that  $\text{ClO}_4$  has a greater migration velocity than  $\text{IO}_4$ . In general, the more complex the ion, the slower its migration velocity. Especially is this the case with the anions of organic acids. With isomeric anions, however, the velocities are approximately equal. With increasing increments of  $\text{CH}_2$  the velocity decreases regularly. The same may be said with regard to the organic cations.

It has been proved by Jones and Getman and by Loomis<sup>2</sup> that organic acids are not hydrated. It is clear that increase in ionic volume is accompanied by decrease in ionic speed, doubtless due to increase in friction between ion and solvent.

With this idea in mind, and with the evidence from the freezing-point measurements that the ions form more and more complex hydrates with increasing dilution, we are forced to believe that the conductivities of solutions of strong electrolytes are less than they would be, theoretically, if there were no hydration, by an amount which is a function of the volume of the ionic complex.

Vollmer<sup>3</sup> determined the values of  $\mu_\infty$  for solutions of potassium acetate, sodium acetate, potassium iodide, lithium iodide, lithium chloride, and silver nitrate, in water and alcohol. He found the relation  $\frac{\lambda'_{\infty \text{ alc}}}{\lambda_{\infty \text{ water}}} = K = 0.33$  to hold in every case.

Kawalki<sup>4</sup> found the same relation to exist between the speeds of diffusion of the same electrolytes in water and alcohol. It is of especial interest to note that the value which he obtained for his constant  $\frac{D'_{\text{alc}}}{D_{\text{water}}} = K' = 0.33$  is the same as that found by Vollmer for conductivity. From their results we obtain the relation

$$\lambda'_{\infty} : \lambda_{\infty} :: D' : D$$

<sup>1</sup>Lehrbuch, 2, 679.

<sup>2</sup>Wied. Ann., 60, 523 (1897).

<sup>3</sup>Ibid., 52, 328 (1894).

<sup>4</sup>Wied. Ann., 52, 300 (1894).



That this relation will hold, in case there is hydration or alcoholation, is highly probable, since the resistance offered to the ionic complex will be the same in each case.

As stated by Jahn,<sup>1</sup> "recent measurements have made it probable that the mobility of the ions is not independent of their concentration, that they have greater mobility in more concentrated than in more dilute solutions." Reference to the work of Jones and Bassett<sup>2</sup> shows that this is just what we should expect. They found, by freezing-point measurements, that the hydration per gram-molecule of the electrolyte decreases with increasing concentration to a certain concentration corresponding to the minimum in the molecular lowering of the freezing-point, and then decreases very slowly with increasing concentration. In the more concentrated solutions, then, we have smaller changes in hydration; therefore, smaller changes in the ionic volumes; hence we should have smaller changes in the mobility of the ions.

That the conductivity depends, in no small degree, upon the viscosity of the solution has been known for a long time; yet the simultaneous action of the two conditions, dissociation and viscosity, renders it impossible to separate their effects. No simple relation exists other than that the conductivity decreases with increase in viscosity.

G. Wiedemann<sup>3</sup> first called attention to the fact that the friction which the ions produce in their motion changes in the sense that the fluidity changes. Accordingly, the mobility of the ions should be a function of the fluidity of the solution.

That the conductivity does not depend exclusively upon the fluidity can be seen in the following case: A 1 per cent (by volume) solution of cane-sugar and a 2.2 per cent solution of methyl alcohol have the same internal friction, viz, 1.046, but the conductivity of potassium chloride in a 1 per cent sugar solution is decreased 3 per cent, while in 2.2 per cent methyl alcohol it is decreased 3.85 per cent.

Pissarjewski and Lemcke<sup>4</sup> made the simple assumption that the conductivity is directly proportional to the dissociation, and inversely proportional to the viscosity,

*e. g.*,  $\mu = K \frac{\alpha}{\eta}$ . At maximum dissociation  $K = \mu_{\infty} \eta_{\infty}$ . Therefore the dissociation is

$$\alpha' = \frac{\mu_s \eta_s}{\mu_{\infty} \eta_{\infty}} \text{ and not } \alpha = \frac{\mu_s}{\mu_{\infty}}$$

In the dilutions which they used the  $K$ , calculated from  $\alpha = \frac{\mu_s}{\mu_{\infty}}$ , varies, while  $K$ , calculated from  $\alpha = \frac{\mu_s \eta_s}{\mu_{\infty} \eta_{\infty}}$ , is a constant.

#### OBJECT OF THE INVESTIGATION.

It was our plan in this work to study the relation between the dissociation as measured by the freezing-point and conductivity methods; to determine to just what extent the conductivity of a solution is influenced by the hydration of the ions; and to study the effect of hydration upon the relative velocities of different ions.

Moreover, it was desired to test the reliability of the conductivity method as a means of measuring the dissociation of strong electrolytes.

In order to do this it was found necessary to redetermine as accurately as possible the freezing-point lowerings produced by various solutions of a large number of salts.

<sup>1</sup>Grundriss der Electrochemie, p. 143.  
<sup>2</sup>Amer. Chem. Journ., 32, 534 (1905).

<sup>3</sup>Pogg. Ann., 99, 228 (1856).  
<sup>4</sup>Zeit. phys. Chem., 52, 479 (1906).

The object of the conductivity measurements was to determine the dissociation of the solution in question, as accurately as possible, in order that the theoretical lowering produced by the substance, if there was no hydration, might be calculated.

The freezing-point measurements give us, on the other hand, an exact proportion between the number of dissolved particles, molecules, ions, or the hydrates of these, and the number of molecules of the solvent acting as such.

#### EXPERIMENTAL.

*Freezing-point Apparatus.*—For all concentrations, from the most dilute up to those which could not be frozen by mixtures of salt and ice, a bath of rather large dimensions was used. The outer cylindrical vessel was made of heavy galvanized iron—diameter 31 cm., depth 26 cm.—covered on the outside by a heavy coat of felt to prevent radiation. Within this was a much smaller vessel of the same material with a tightly fitting cover. Soldered around the large hole in the center of the cover is a conical-shaped collar, which holds firmly the cork through which the thermometer is inserted. By this means the thermometer always reaches to the same depth in the solution. A second smaller hole in the side is provided for the passage of the stirrer. To the bottom and on the outside was soldered a short bolt, which, in turn, was screwed into a nut soldered to the center of the outer vessel. In this way firm support was given the inner vessel and danger of floating was avoided. The freezing-tube proper was a large glass tube—length 17 cm., diameter 5.5 cm., of 250 c.c. capacity. It was supported within the smaller vessel at the bottom by a cork, and at the top by a cork ring which rested upon an iron ledge soldered to the inside of the small vessel. These dimensions allowed for an air-space of about 2 cm. all around.

The stirrer consisted of a gold-plated brass disk, with one large hole in the center to permit the passage of the thermometer, and around this smaller holes about 0.7 cm. in diameter.

Near the top of the large outer cylinder was soldered a small tube which served to keep the water in the bath at constant level.

By means of a bath of these dimensions the temperature of the freezing-mixture could be kept constant for five or six hours. No attempt was made to control exactly the temperature of the bath, but experience taught us that only those freezing-mixtures which required from forty seconds to one minute to cool the solution  $0.1^{\circ}\text{C}$ . could be depended upon for reliable results.

For solutions requiring freezing-mixtures of calcium chloride, and in the ordinary cryoscopic apparatus consisting of a battery jar, two test-tubes were used.

For this work four thermometers of the Beckmann type were employed, whose temperature ranges were  $1.1^{\circ}$ ,  $5.6^{\circ}$ ,  $12.2^{\circ}$ , and  $25^{\circ}\text{C}$ . These were graduated into  $0.002^{\circ}$ ,  $0.01^{\circ}$ ,  $0.02^{\circ}$ , and  $0.05^{\circ}$ , respectively (whole scale). By means of a lens it was easy to read to a tenth of the above graduations.

#### CONDUCTIVITY.

The conductivity measurements were made by means of the well-known Kohlrausch method, using the Wheatstone bridge, induction coil, and telephone receiver.

The wire was calibrated according to the method of Strouhal and Barus.<sup>1</sup> The resistance coils were made by Leeds, of Philadelphia, and had been carefully calibrated. Conductivity cells of two types were used. For the more dilute solutions cells of the type devised by Jones and Bingham<sup>2</sup> were employed. For the more concentrated solutions U-shaped cells, similar to those used by Jones and Getman,<sup>3</sup> were found to be very convenient.

All conductivity measurements were made at 0° C. For this purpose a small pail was filled with finely crushed ice, moistened with distilled water, and the cells packed into the ice as tightly as possible. The small pail was then placed in a spacious pan and the space between the pail and the pan filled with finely crushed ice.

#### SPECIFIC GRAVITY.

Since the solutions were made up at 20°, we thought it best to determine their specific gravities at the same temperature. The 20° bath was a large galvanized-iron tub. By means of a very small flame below, and a stirrer within, driven by a hot-air motor, the temperature could easily be kept to within 0.1° of the desired temperature. Throughout this work six pycnometers of the Ostwald type were employed. They were carefully calibrated with pure, redistilled water.

The flasks and burettes used in this work were carefully calibrated at 20° by the method of Morse and Blalock.<sup>4</sup>

#### SOLUTIONS AND SOLVENT.

Kahlbaum's "chemically pure" materials were used in every case, and were further purified whenever it was found desirable to do so. The method of preparing the solutions varied according to the solute employed. In general, a solution of slightly greater concentration than 2 normal was first made, and from this, by successive dilutions, the lesser concentrations were obtained. Whenever possible, the mother-solution was made up by direct weighing; when the nature of the solute did not permit it to be weighed, the mother-solution was diluted to convenient strength, and portions of the dilute solution were standardized either by gravimetric or volumetric methods.

The water which was used in all the solutions was purified according to the method of Jones and Mackay.<sup>5</sup> Ordinary distilled water was twice redistilled from an acidified solution of potassium dichromate, and the steam from the second distillation passed through a boiling solution of barium hydroxide. It had, at 0°, a conductivity of about  $1.2 \times 10^{-6}$  to  $1.7 \times 10^{-7}$ .

#### CALCULATION OF THE COMPOSITION OF THE HYDRATES.

The method of calculating the amount of water combined with the dissolved substance is essentially the same as that used by Jones and Bassett.<sup>6</sup> We have given the observed molecular lowering of the freezing-point, the specific gravity of the solutions, and the dissociation. The observed molecular lowering is corrected for the difference between 1,000 grams and the amount of water actually present in 1 liter of the solution. This gives the true molecular lowering which would be produced by the substance at the dilution in question if there were 1,000 grams of water present.

<sup>1</sup>Wied. Ann., 10, 326 (1880).

<sup>2</sup>Amer. Chem. Journ., 34, 451 (1905).

<sup>3</sup>Zeit. phys. Chem., 46, 244 (1903).

<sup>4</sup>Amer. Chem. Journ., 16, 479 (1904).

<sup>5</sup>Ibid., 19, 83 (1897).

<sup>6</sup>Ibid., 33, 843 (1905); 34, 298 (1906).

From the dissociation we calculate the true molecular lowering which would be produced by the dissolved substances if there were no hydration; and if there is no hydration these two values for the molecular lowering should be equal.

The calculated lowering, divided by the observed lowering and multiplied by 1,000, gives the amount of water present playing the rôle of solvent, if the quantity of the substance present is dissolved in 1,000 grams of water.

The difference between this amount of water and 1,000 grams gives the amount of water which is combined with the dissolved substance in the solution in question.

Knowing the number of grams of water which are in combination with the dissolved substance, the number of gram-molecules of water combined with the substance is obtained by dividing this number by 18. If we divide this value by the concentration in terms of normal, we obtain the number of molecules of water which are in combination with one molecule of the dissolved substance when the amount of substance present in 1 liter of the solution is dissolved in 1,000 grams of water.

In the various tables of data the symbols have the significance already stated.

In the specific-gravity tables,  $W_{sol}$  is the weight of 1 liter of the solution;  $W_{salt}$  is the weight of the salt contained in 1 liter of the solution; and  $W_{H_2O}$  is the weight of water contained in 1 liter of the solution. The percentage correction is the correction which must be applied to the freezing-point lowering in order to refer it to 1,000 grams of the solvent, instead of the amount of water that is actually present in 1 liter of the solution in question.

In the hydrate tables,  $m$  is the concentration in gram-molecules per liter;  $a$  the approximate dissociation as measured by the conductivity method;  $L$  the theoretical molecular lowering of the freezing-point referred to 1,000 grams of solvent;  $\Delta/m$  the observed molecular lowering;  $L'$  the corrected molecular lowering;  $M$  the number of gram-molecules of water in combination with the solute; and  $H$  the number of gram-molecules of water combined with one molecule of the salt at the concentration in question.

#### CALCIUM CHLORIDE.

The data for calcium chloride are given in table 45.

The value of  $\mu_\infty$  is surprisingly low when compared with that obtained by West<sup>1</sup> and by Bassett.<sup>2</sup> It is however, very nearly equal to that obtained by Jones and Stine.<sup>3</sup>

A study of table 45 leads us to the following conclusions: The theoretical molecular lowerings, as given in column  $L$ , decrease regularly with increase in concentration, while the corrected observed molecular lowerings, as seen in column  $L'$ , decrease rapidly, reach a minimum at 0.1 normal, and then increase with increase in concentration.

It is very probable that the value of  $L'$  for 0.01 normal is too large, but, owing to the inaccuracy of the method for such dilutions, this is unavoidable.

It will be seen from column  $M$  that the amount of water which has entered into combination with the dissolved salt also passes through a minimum between 0.075 normal and 0.10 normal—the same concentration which gives the minimum molec-

<sup>1</sup>Amer. Chem. Journ., 34, 393 (1905).

<sup>2</sup>Ibid., 33, 547 (1905).

<sup>3</sup>Ibid., 39, 331 (1908).

ular lowering of the freezing-point. A similar minimum was noted by Jones and Bassett<sup>1</sup> for concentrations ranging from 0.102 normal to 0.153 normal. It has been

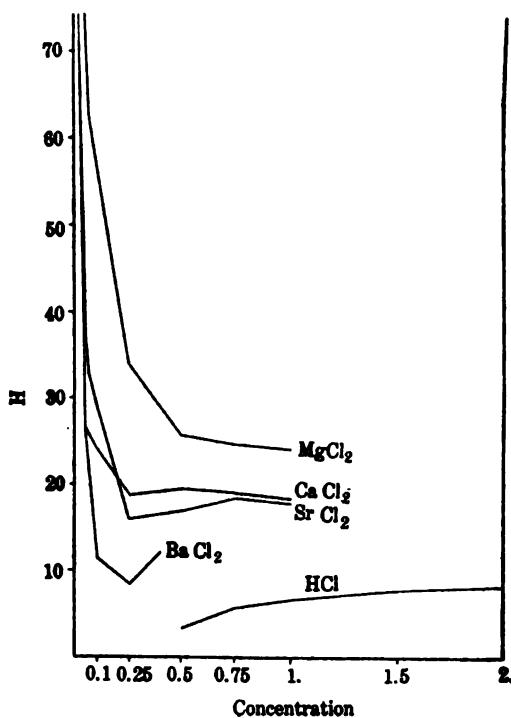


FIG. 22.

assumed hitherto, by Jones and his coworkers, that the minimum in the freezing-point lowering always occurs in that concentration where the effect due to decrease in dissociation is just counterbalanced by the effect due to hydration. The values of  $L'$  and  $M$  also show that the abnormality of the freezing-point lowering is greatly augmented by the relatively great hydrating power of the ions, since it is the ions with which we are chiefly concerned in the dilute solutions. A glance at column  $H$  shows us at once the great hydrating power of the ions in dilute solution. The values of  $H$  decrease regularly with increase in concentration to 0.10 normal. From that concentration on, the decrease in hydration is very slight as the concentration increases. In these concentrations the combined effect upon the freezing-point lowering, due both to the dissociation and to the hydration

of the ions, is small, compared with the effect due to the undissociated molecules.

If we refer to the literature<sup>2</sup> bearing upon the relation between the water of crystallization of a salt and the temperature at which it crystallizes we see that, over a definite range of temperature, the amount of water of crystallization is constant. If, then, we eliminate the hydration due to the ions, we should expect to find the number of molecules of water combined with one molecule of the salt to be a constant for a definite range of temperature. This is clearly shown by the values of  $H$  for the more concentrated solutions.

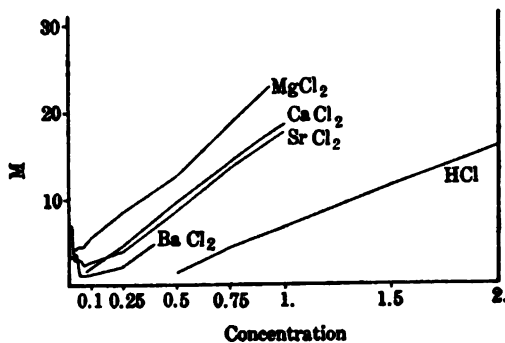


FIG. 23.

The values of  $M$  are plotted in fig. 23 against the concentrations as abscissæ. The curve shows, at a glance, that the amount of water held in combination from the dilution at which the minimum occurs is a linear function of the concentration.

<sup>1</sup>Amer. Chem. Journ., 33, 548 (1905).

<sup>2</sup>Bassett: *Ibid.*, 34, 294 (1905).

The values of  $H$  are plotted in the curve (fig. 22) against the concentration as abscissas. An explanation regarding these hydrate curves is necessary at this point. With one or two exceptions, it was found impossible to plot on the paper the values of  $H$  for the more dilute solutions.

These curves show the rapid decrease in hydration until the minimum is reached, and then a very slight decrease with increasing concentration.

TABLE 45.—Calcium Chloride—Data for Freezing-point and Conductivity Measurements, Specific Gravity, and Hydrates.

Freezing-point.					Hydrates.						
<i>m</i>	$\Delta$	$\Delta/m$	<i>i</i>	<i>a</i>	<i>m</i>	<i>a</i>	<i>L</i>	$\Delta/m$	<i>L'</i>	<i>M</i>	<i>H</i>
0.01	0.05945	5.9450	.....	.....	.....	.....	.....	.....	.....	.....	.....
0.025	0.1318	5.2720	2.8344	91.72	0.025	84.37	4.9885	5.2720	5.2708	2.869	114.7
0.05	0.2511	5.0220	2.7000	85.00	0.05	80.62	4.7590	5.0220	5.0187	2.874	57.4
0.075	0.3651	4.8690	2.6177	80.88	0.075	76.60	4.7095	4.8690	4.8617	1.742	23.2
0.10	0.48515	4.8515	2.6083	80.41	0.10	74.35	4.6258	4.8515	4.8414	2.474	24.7
0.25	1.2335	4.9340	2.6526	.....	0.25	70.62	4.487	4.934	4.910	4.785	19.1
0.50	2.6270	5.2540	2.8247	.....	0.5	65.39	4.293	5.254	5.197	9.663	19.3
0.75	4.1955	5.5940	3.0075	.....	0.75	60.49	4.110	5.594	5.501	14.048	18.7
1.00	6.1040	6.1040	3.2817	.....	1.00	57.49	3.998	6.104	5.962	18.30	18.3

Conductivity. $\mu_{\infty} 0 = 123.46$ .			Specific gravity.					
<i>V</i>	$\mu_s$	<i>a</i>	<i>m</i>	Sp. gr.	<i>W</i> <sub>sol</sub>	<i>W</i> <sub>salt</sub>	<i>W</i> <sub>H<sub>2</sub>O</sub>	Correction, per cent.
100	111.23	89.67	0.01	1.00098	1000.98	1.109	999.873	0.012
40	104.66	84.37	0.025	1.00254	1002.53	2.772	999.767	0.023
20	100.01	80.62	0.05	1.00487	1004.87	5.545	999.329	0.067
13.34	95.02	76.60	0.075	1.00681	1006.81	8.317	998.497	0.150
10	92.23	74.35	0.10	1.00897	1008.97	11.090	997.881	0.211
4	87.19	70.62	0.25	1.02267	1022.67	27.725	994.954	0.504
2	80.73	65.39	0.50	1.04451	1044.51	55.450	989.06	1.094
1.334	74.69	60.49	0.75	1.06641	1066.41	83.175	983.23	1.676
1.00	70.98	57.49	1.00	1.08744	1087.44	110.900	976.54	2.345

#### STRONTIUM CHLORIDE.

The concentrated mother-solution was diluted to convenient strength and equal portions were taken for standardization. The strontium was precipitated and weighed as strontium carbonate.

The conductivity measurements for this salt gave, at maximum dissociation,  $\mu_{\infty} = 128.57$ . The corresponding value obtained by Jones and Stine was  $\mu_{\infty} = 128.44$ .

The minimum in the freezing-point lowerings (column  $L'$ ) is found at 0.25 normal, whereas the minimum in the total combined water occurs at a somewhat greater dilution (0.05 normal). The values of  $H$  become approximately constant at 0.25 normal, the minimum point in the freezing-point lowering.

The values of  $m$  and  $H$  for calcium and strontium chlorides, tables 45 and 46, show numbers of approximately the same order of magnitude. For curves, see figs. 22 and 23.

As in the case of calcium chloride, the values of the theoretical lowerings ( $L$ ) are less than the observed lowerings ( $L'$ ) in every instance.

TABLE 46.—Strontium Chloride—Data for Freezing-point and Conductivity Measurements, Specific Gravity, and Hydrates.

Freezing-point.					Hydrates.						
<i>m</i>	$\Delta$	$\Delta/m$	<i>i</i>	$\alpha$	<i>m</i>	$\alpha$	<i>L</i>	$\Delta/m$	<i>L'</i>	<i>M</i>	<i>H</i>
0.01	0.05273	5.2730	2.8351	91.87	0.01	89.37	5.1845	5.2733	5.2718	.....	.....
0.02937	0.1550	5.2800	2.8386	91.93	0.02937	82.56	4.9312	5.2800	5.2763	3.634	123.6
0.03987	0.2028	5.0752	2.7382	86.91	0.03987	80.32	4.8479	5.0752	5.0705	2.439	61.2
0.5011	0.2476	4.9349	2.6531	82.65	0.05017	78.08	4.7645	4.9349	4.9304	1.871	37.2
0.7077	0.3472	4.9060	2.6376	81.88	0.07077	76.27	4.6982	4.9060	4.8977	2.274	32.13
0.10	0.48904	4.8904	2.6292	81.46	0.10	74.17	4.6191	4.8904	4.8803	2.973	29.73
0.25	1.1957	4.7830	2.5715	78.57	0.25	68.59	4.4115	4.7830	4.7582	4.047	16.18
0.50	2.5339	5.0678	2.7354	.....	0.50	63.96	4.2393	5.0678	5.0127	8.572	17.14
0.75	4.0989	5.4652	2.9385	.....	0.75	58.30	4.0287	5.4652	5.3718	13.890	18.52
1.00	5.9211	5.9211	3.1833	.....	1.00	55.47	3.9234	5.9211	5.7844	17.873	17.87

Conductivity. $\mu_{\infty} 0^{\circ} = 123.57$ (Stine 123.4).			Specific gravity.					
<i>V</i>	$\mu_s$	$\alpha$	<i>m</i>	Sp. gr.	<i>W</i> <sub>sol</sub>	<i>W</i> <sub>salt</sub>	<i>W</i> <sub>H<sub>2</sub>O</sub>	Correction, per cent.
1100	123.57	.....	0.01	1.001228	1001.2284	1.585	999.7034	0.029
550	127.99	.....	0.02937	1.003839	1003.9396	4.6559	999.2837	0.071
100	115.64	89.37	0.03987	1.005383	1005.3832	6.3197	999.0635	0.093
34.04	106.10	82.66	0.05017	1.007028	1007.028	7.952	999.078	0.092
25.08	103.26	80.32	0.07077	1.00956	1009.516	11.217	998.299	0.170
19.93	101.04	78.08	0.10	1.013205	1013.215	15.85	997.930	0.207
14.03	98.06	76.27	0.25	1.034433	1034.433	38.625	994.808	0.519
10	95.98	74.17	0.5	1.068379	1068.379	79.250	989.129	1.087
4	88.07	68.59	0.75	1.101760	1101.160	118.875	982.885	1.711
2	82.18	63.96	1.00	1.135423	1135.423	158.50	976.923	2.308
1.333	74.86	58.30						
1.0	71.23	55.47						

## MAGNESIUM CHLORIDE.

The value of  $\mu_{\infty}$  for magnesium chloride was found to be 123.95. The values of *L'* show a minimum at 0.25 normal, while the values of *H* begin to be constant at 0.5 normal. Magnesium chloride differs from the other chlorides thus far discussed in that its values for *M* show no minimum, but increase regularly with increasing concentration. (See table 47.)

It should be noticed also that magnesium chloride has greater power to combine with water than any of the halides of the calcium group. Especially is this the case in the dilute solutions, where the ions predominate. That this is not due to hydrolysis and the liberation of the free mineral acid is evident from the fact that the molecular lowering of the freezing-point in the dilute solutions is in every case considerably higher than the calculated lowering. As we shall see later, in our study of the acids just the reverse was found to be the case. The curves for this salt are found in figs. 22 and 23.

## BARIUM CHLORIDE.

A nearly saturated solution of this salt was first made. This was diluted to convenient concentration, and equal portions were precipitated and weighed as barium sulphate. Owing to the slight solubility of this salt, we did not attempt to work with concentrations greater than 0.4 normal.

TABLE 47.—*Magnesium Chloride—Data for Freezing-point and Conductivity Measurements, Specific Gravity, and Hydrates.*

Freezing-point.					Hydrates.						
<i>m</i>	$\Delta$	$\Delta/m$	<i>i</i>	<i>a</i>	<i>m</i>	<i>a</i>	<i>L</i>	$\Delta/m$	<i>L'</i>	<i>M</i>	<i>H</i>
0.004928	0.02741	5.5630	2.9909	99.54	0.01	90.90	5.2415	5.4720	5.4714	2.334	233.4
0.007317	0.04072	5.5643	2.9916	99.58	0.03104	83.16	4.9535	5.3581	5.3570	4.185	134.82
0.01	0.05472	5.4720	2.9420	97.10	0.05108	79.78	4.8278	5.2443	5.2407	4.377	85.69
0.05108	0.2678	5.2443	2.8195	90.75	0.07171	76.93	4.7218	5.1421	5.1381	4.501	62.76
0.07171	0.3687	5.1421	2.7651	88.25	0.10	73.61	4.5982	5.1330	5.1278	5.737	57.37
0.09986	0.5133	5.1330	2.7596	87.68	0.25	65.72	4.1675	4.9408	4.9268	8.562	34.24
0.25	1.2352	4.9408	2.6563	82.81	0.50	59.50	4.0734	5.3536	5.3049	12.898	25.79
0.50	2.6768	5.3536	2.8783	.....	0.75	53.63	3.8550	5.9104	5.8247	18.787	25.05
0.75	4.4328	5.9104	3.1776	.....	0.9415	48.66	3.6701	6.4385	6.3098	23.242	24.68
0.9415	6.0619	6.4885	3.4615	.....	.....	.....	.....	.....	.....	.....	.....

Conductivity. $\mu_{\infty} 0^{\circ}=123.95$ .			Specific gravity.					
<i>V</i>	$\mu_s$	<i>a</i>	<i>m</i>	Sp. gr.	<i>W</i> <sub>sol</sub>	<i>W</i> <sub>salt</sub>	<i>W</i> <sub>H<sub>2</sub>O</sub>	Correction, per cent.
402.25	120.15	96.94	0.00493	1.00034	1000.344	0.4695	999.875	0.012
202.92	116.67	94.13	0.007317	1.00052	1000.524	0.6970	999.827	0.017
136.67	113.86	91.86	0.01	1.00084	1000.842	0.9526	999.889	0.012
100.0	112.68	90.90	0.03104	1.00276	1002.756	2.9568	999.799	0.020
32.21	103.08	83.16	0.05108	1.00422	1004.224	4.9168	999.30	0.069
19.57	98.88	79.78	0.07171	1.00604	1006.036	6.8316	999.204	0.079
13.94	95.36	76.93	0.100	1.00850	1008.505	9.5260	998.979	0.102
10.0	91.25	73.61	0.25	1.02097	1020.966	23.8150	997.151	0.284
4.0	80.22	64.72	0.50	1.03850	1038.496	47.630	990.866	0.910
2.0	72.07	59.50	0.75	1.05690	1056.905	71.445	985.460	1.450
1.333	64.69	53.63	0.9415	1.06962	1069.617	89.689	979.930	2.007
1.062	60.31	48.66	.....	.....	.....	.....	.....	.....

TABLE 48.—*Barium Chloride—Data for Freezing-point and Conductivity Measurements, Specific Gravity, and Hydrates.*

Freezing-point.					Hydrates.						
<i>m</i>	$\Delta$	$\Delta/m$	<i>i</i>	<i>a</i>	<i>m</i>	<i>a</i>	<i>L</i>	$\Delta/m$	<i>L'</i>	<i>M</i>	<i>H</i>
0.01	0.5463	5.4630	2.9370	96.85	.....	.....	.....	.....	.....	.....	.....
0.025	1.3398	5.3592	2.8813	94.06	0.025	84.16	4.9907	5.3592	5.3568	3.796	151.8
0.05	0.24770	4.9551	2.6639	83.19	0.05	80.09	4.8393	4.9551	4.9496	1.238	24.7
0.075	0.36128	4.8171	2.5898	79.49	0.075	76.24	4.6961	4.8171	4.8080	1.293	17.2
0.10	0.4792	4.7925	2.5766	78.83	0.10	75.65	4.6742	4.7925	4.7772	1.197	11.9
0.25	1.1669	4.6677	2.5095	75.47	0.25	69.79	4.4562	4.6677	4.6374	2.172	8.69
0.40	1.902	4.7370	2.5575	.....	0.40	65.35	4.2910	4.7570	4.7061	4.900	12.25

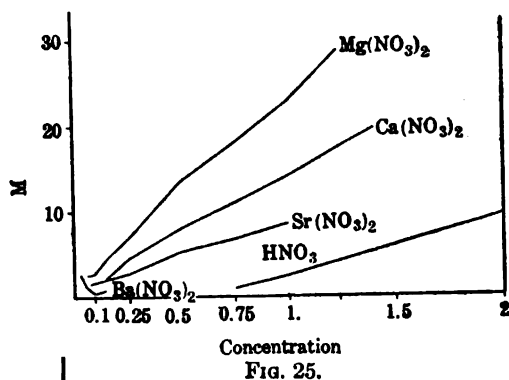
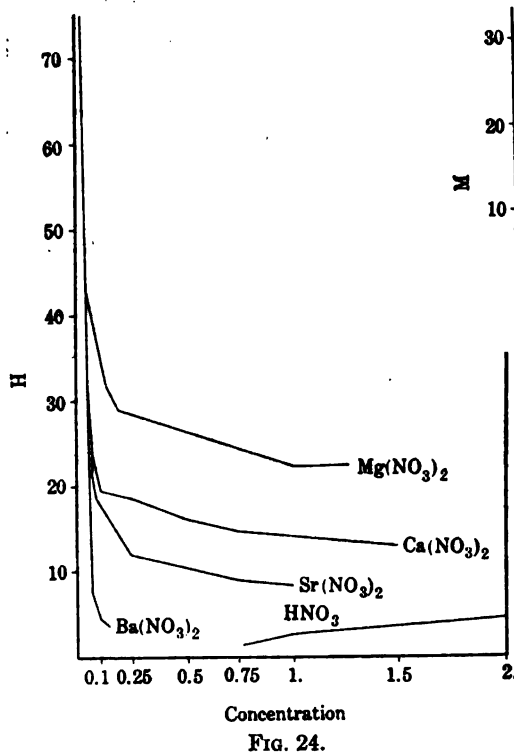
Conductivity. $\mu_{\infty}=132.07$ .			Specific gravity.					
<i>V</i>	$\mu_s$	<i>a</i>	<i>m</i>	Sp. gr.	<i>W</i> <sub>sol</sub>	<i>W</i> <sub>salt</sub>	<i>W</i> <sub>H<sub>2</sub>O</sub>	Correction, per cent.
100	120.01	90.87	0.01	1.00188	1001.87	2.063	999.795	0.021
40	111.15	84.16	0.025	1.00475	1004.75	5.207	999.545	0.045
20	105.78	80.09	0.05	1.00929	1009.29	10.415	998.879	0.112
13.33	100.69	76.24	0.075	1.01369	1013.69	15.622	998.074	0.197
10	99.92	75.65	0.10	1.01766	1017.66	20.830	996.830	0.316
4	92.18	69.79	0.25	1.0456	1045.61	52.075	993.542	0.645
2.5	86.31	65.35	0.40	1.0726	1072.65	83.320	989.335	1.066



Conductivity measurements gave us the value  $\mu_{\infty} = 132.07$ .

What has been said regarding the chlorides of calcium, strontium, and magnesium applies equally well to barium chloride. The low value of  $H$  for 0.25 normal is doubtless due to experimental error. (Table 48.)

It is interesting to note that while the molecules of barium chloride have a much smaller hydrating power than the other chlorides of the alkaline earth metals, as we should expect from the fact that it crystallizes with but two molecules of water, the ions which predominate in the dilute solutions have a relatively high hydrating power.



Another point is to be noted—one to which reference will be made later in this paper. A glance at the curves representing the values of  $M$  and  $H$  for the three salts—calcium, strontium, and magnesium chlorides—will show that in each case the curves for calcium chloride lie above those for strontium chloride, while the two curves for magnesium chloride lie above those for calcium chloride. *This order is just*

*the reverse of that for the atomic volumes of the three metals.* Although barium chloride crystallizes with but two molecules of water, the atomic volume of barium is still larger than that of strontium. This may account for the relatively high hydrating power of the ions of barium salts.

The curves for the values of  $M$  and  $H$  are given in figs. 23 and 22, respectively.

#### CALCIUM NITRATE.

The mother-solution was diluted and 50 c.c. portions were taken for standardization. The calcium was precipitated by means of ammonium oxalate and weighed as calcium oxide. Table 49 gives the data; the curves are plotted in figs. 24 and 25.

Nothing special need be said regarding the data for calcium nitrate, except to call attention to the fact that the amounts of water combined with calcium chloride in

TABLE 49.—*Calcium Nitrate—Data for Freezing-point and Conductivity Measurements, Specific Gravity, and Hydrates.*

Freezing-point.					Hydrates.						
<i>m</i>	$\Delta$	$\Delta/m$	<i>i</i>	<i>a</i>	<i>m</i>	<i>a</i>	<i>L</i>	$\Delta/m$	<i>L'</i>	<i>M</i>	<i>H</i>
0.0125	0.072	5.7560	.....	.....	0.025	81.13	4.8780	5.2120	5.2072	3.511	140.4
0.025	0.1303	5.2120	2.8021	90.10	0.05	76.00	4.6872	4.8090	4.7986	1.288	25.7
0.05	0.2405	4.8090	2.5855	79.27	0.125	67.66	4.3769	4.6019	4.5776	2.437	19.5
0.125	0.5752	4.6019	2.4736	73.68	0.25	61.28	4.139	4.569	4.522	4.703	18.8
0.25	1.1424	4.5695	2.4567	72.83	0.5	52.52	3.813	4.572	4.471	8.173	16.3
0.05	2.2860	4.5720	2.4580	.....	0.75	46.03	3.572	4.645	4.485	11.312	15.07
0.75	3.484	4.645	2.4974	.....	1.00	40.49	3.366	4.766	4.544	14.490	14.49
1.0	4.766	4.766	2.5623	.....	1.5	31.75	3.041	5.077	4.709	19.683	13.12
1.5	7.616	5.077	2.7299	.....							
Conductivity. $\mu_{\infty}0^{\circ}=126.60.$					Specific gravity.						
<i>V</i>	$\mu_s$	<i>a</i>	<i>m</i>	Sp. gr.	<i>W</i> <sub>sol</sub>	<i>W</i> <sub>sat</sub>	<i>W</i> <sub>H<sub>2</sub>O</sub>	Correction, per cent.			
0.80	108.60	85.72	0.0125	1.00185	1001.84	2.052	999.794	0.021			
0.40	102.78	81.13	0.025	1.00317	1003.16	4.104	999.062	0.094			
0.20	96.28	76.00	0.05	1.00604	1006.04	8.209	997.831	0.217			
8.0	85.72	67.66	0.125	1.01523	1015.23	20.520	994.71	0.529			
4.0	77.64	61.28	0.25	1.03074	1030.74	41.04	989.70	1.030			
2.0	66.54	52.52	0.5	1.06011	1060.11	82.09	978.02	2.198			
1.333	58.32	46.03	0.75	1.08874	1008.74	123.13	965.61	3.439			
1.00	51.30	40.49	1.00	1.11751	1117.51	164.18	953.33	4.66			
0.6667	40.24	31.75	1.5	1.17375	1173.75	246.27	927.48	7.25			

TABLE 50.—*Strontium Nitrate—Data for Freezing-point and Conductivity Measurements, Specific Gravity, and Hydrates.*

Freezing-point.					Hydrates.						
<i>m</i>	$\Delta$	$\Delta/m$	<i>i</i>	$\alpha$	<i>m</i>	$\alpha$	<i>L</i>	$\Delta/m$	<i>L'</i>	<i>M</i>	<i>H</i>
0.01	0.05717	5.7170	3.0736	103.68	.....	.....	.....	.....	.....	.....	.....
0.025	0.1304	5.2180	2.8053	90.27	0.025	80.36	4.8493	5.7180	5.7124	3.870	154.8
0.05	0.2402	4.8050	2.5833	79.16	0.05	74.92	4.6470	4.8050	4.7945	1.710	34.20
0.075	0.3492	4.6567	2.5036	75.18	0.075	71.06	4.5034	4.6567	4.6418	1.657	22.09
0.10	0.4587	4.5875	2.4664	73.32	0.10	68.59	4.4115	4.5875	4.5677	1.900	19.00
0.25	1.0817	4.326	2.3263	66.31	0.25	58.58	4.0391	4.3269	4.2798	3.124	12.49
0.5	2.0849	4.169	2.2418	62.09	0.5	48.83	3.676	4.169	4.075	5.437	10.87
0.75	3.0453	4.060	2.1829	59.15	0.75	42.01	3.422	4.060	3.918	7.030	9.37
1.00	3.9983	3.9983	2.1496	57.48	1.00	36.37	3.213	3.998	3.806	8.607	8.65

Conductivity. $\mu_{\infty}0^{\circ}=125.62.$			Specific gravity.					
<i>V</i>	$\mu_s$	$\alpha$	<i>m</i>	Sp. gr.	<i>W</i> <sub>sol</sub>	<i>W</i> <sub>sat</sub>	<i>W</i> <sub>H<sub>2</sub>O</sub>	Correction, per cent.
100	111.14	88.47	0.01	1.00152	1001.525	2.116	999.409	0.059
40	100.95	80.36	0.025	1.00421	1004.207	5.292	998.915	0.108
20	94.12	74.92	0.05	1.00839	1008.391	10.584	997.807	0.219
13.34	89.26	71.06	0.075	1.01265	1012.646	15.876	996.770	0.323
10	86.16	68.59	0.10	1.01683	1016.834	21.168	995.666	0.433
4	73.59	58.58	0.25	1.04201	1042.01	52.92	989.09	1.09
2	61.34	48.83	0.50	1.08312	1088.12	105.84	977.28	2.27
1.33	52.77	42.01	0.75	1.12386	1123.86	158.76	965.11	3.48
1	45.69	36.37	1.00	1.16354	1163.54	211.68	951.86	4.81

solution are, in general, higher than the amounts combined with calcium nitrate. This is just what we should expect when we consider that calcium chloride crystallizes with 6 molecules of water, while calcium nitrate crystallizes with 4.

#### STRONTIUM NITRATE.

The strontium was precipitated and weighed as the carbonate. Unlike the other salts thus far studied, the freezing-point lowerings show no minimum within the range of concentrations used, the molecular lowering constantly decreasing in value. A minimum was, however, obtained by Jones and Bassett<sup>1</sup> at a concentration of about 1.5 normal. The data are given in table 50.

The values for the combined water show a minimum at 0.075 normal, just as calcium nitrate does. The hydration per ion and the molecule also shows no tendency to become constant. The curves are plotted in figs. 24 and 25.

#### MAGNESIUM NITRATE.

The nitrate of magnesium, like the chloride, shows a much greater power to combine with water, throughout the range of concentration studied, than do the nitrates of the alkali earth metals. (Table 51.)

TABLE 51.—*Magnesium Nitrate—Data for Freezing-point and Conductivity Measurements, Specific Gravity, and Hydrates.*

Freezing-point.					Hydrates.						
<i>m</i>	$\Delta$	$\Delta/m$	<i>i</i>	<i>a</i>	<i>m</i>	<i>a</i>	<i>L</i>	$\Delta/m$	<i>L'</i>	<i>M</i>	<i>H</i>
0.02	0.1078	5.3903	2.8980	94.90	0.05	78.80	4.7913	4.9938	4.9849	2.157	43.14
0.05	0.24968	4.9938	2.6848	84.24	0.10	74.78	4.6418	4.9085	4.8903	2.817	28.17
0.10	0.49085	4.9085	2.6390	81.95	0.15	71.40	4.5161	4.9671	4.9388	4.759	31.73
0.15	0.74486	4.9671	2.6705	83.52	0.20	69.25	4.4361	4.9937	4.9555	5.819	29.09
0.20	0.99875	4.9937	2.6848	.....	0.50	60.07	4.0946	5.4856	5.3792	13.260	26.52
0.50	2.74280	5.4856	2.9492	.....	1.00	49.43	3.6988	6.5145	6.2507	22.672	22.67
1.00	6.5145	6.5145	3.5024	.....	1.274	44.46	3.5139	7.1032	6.7303	29.006	22.76

Conductivity. $\mu_{\infty}0^{\circ}=119.90$ .			Specific gravity.					
<i>V</i>	$\mu_v$	<i>a</i>	<i>m</i>	Sp. gr.	<i>W</i> <sub>sol</sub>	<i>W</i> <sub>rat</sub>	<i>W</i> <sub>H<sub>2</sub>O</sub>	Correction, per cent.
50	102.06	85.12	0.02	1.00224	1002.224	2.968	999.255	0.074
20	94.48	78.80	0.05	1.00563	1005.626	7.422	998.204	0.179
10	89.66	74.78	0.10	1.01112	1011.118	14.844	996.274	0.372
6.666	85.61	71.40	0.15	1.01656	1016.557	22.266	994.291	0.571
5	83.04	69.25	0.20	1.02203	1022.026	29.688	992.338	0.766
2	72.03	60.07	0.50	1.05480	1054.804	74.220	980.584	1.941
1	59.27	49.43	1.00	1.10786	1107.865	148.440	959.425	4.057
.....	.....	.....	1.274	1.13661	1136.615	189.112	947.502	5.249

The amount of water decreases with increase in concentration in the dilute solutions, reaches a minimum at 0.05 to 0.075 normal, and then increases regularly with increase in concentration. The values of *H* do not approach a constant until normal concentration is reached. It is very probable that the relatively low values of *H* for 0.05 and 0.1 normal are due to errors in measuring the freezing-points of those solutions. The curves for magnesium nitrate are given in figs. 24 and 25.

<sup>1</sup>Amer. Chem. Journ., 34, 305 (1905).

## BARIUM NITRATE.

Owing to the very small solubility of this salt we did not attempt to make measurements beyond 0.15 normal. Barium nitrate has special interest in that it is the first salt thus far studied in this investigation which, under ordinary conditions, crystallizes without water.

TABLE 52.—*Barium Nitrate—Data for Freezing-point and Conductivity Measurements, Specific Gravity, and Hydrates.*

Freezing-point.					Hydrates.						
<i>m</i>	$\Delta$	$\Delta/m$	<i>i</i>	$\alpha$	<i>m</i>	$\alpha$	<i>L</i>	$\Delta/m$	<i>L'</i>	<i>M</i>	<i>H</i>
0.01	0.05545	5.5450	2.9812	99.06	0.05	70.47	4.4814	4.6566	4.6451	1.957	39.15
0.025	0.12482	4.9928	2.6838	84.19	0.075	65.51	4.2969	4.3606	4.3434	0.595	7.93
0.05	0.23281	4.6566	2.5035	75.18	0.10	61.30	4.1425	4.2018	4.1808	0.509	5.09
0.075	0.32704	4.3606	2.3440	67.20	0.10	55.47	3.9234	3.9955	3.9648	0.5805	3.87
0.10	0.42018	4.2018	2.2590	62.95	.....	.....	.....	.....	.....	.....	.....
0.15	0.59935	3.9955	2.1481	57.40	.....	.....	.....	.....	.....	.....	.....

Conductivity. $\mu_{\infty} 0^{\circ}=128.08.$			Specific gravity.					
<i>V</i>	$\mu_s$	$\alpha$	<i>m</i>	Sp. gr.	<i>W</i> <sub>sol</sub>	<i>W</i> <sub>salt</sub>	<i>W</i> <sub>H<sub>2</sub>O</sub>	Correction, per cent.
100	110.62	86.37	0.01	1.00203	1002.031	2.14	999.891	0.088
40	99.04	77.32	0.025	1.00522	1005.224	6.537	998.687	0.131
20	90.26	70.47	0.05	1.01059	1010.591	13.074	997.517	0.248
13.34	83.92	65.51	0.075	1.01567	1015.671	19.611	996.060	0.394
10	78.59	61.36	0.10	1.02114	1021.143	26.148	994.995	0.500
6.67	71.05	55.47	0.15	1.03177	1031.770	39.222	992.548	0.745

It will be seen that, like strontium nitrate, the molecular lowering of the freezing-point decreases regularly as the concentration increases, without showing a minimum value. The amount of water held in combination decreases rapidly and reaches a minimum at 0.1 normal. The hydration per molecule is very small, as we should expect, since the salt in its solid state is anhydrous. In the more dilute solutions, however, where the ions predominate, the hydration is of the same order as that of the other nitrates of the alkali earths. This is, indeed, convincing proof that the ions themselves have great hydrating power.

It was pointed out in the introduction that if there were no hydration the corrected molecular lowering of the freezing-point should be equal to the corrected lowering. A glance at table 52 will show how closely the assumption agrees with facts. The values for the corrected freezing-point lowerings for the three most concentrated solutions, in which the hydration is least, are only about 1 per cent higher than the calculated values. Moreover, if there is no hydration, and if we may disregard the effect of viscosity upon the velocity of the ions, we should expect the dissociation as measured by the conductivity and freezing-point methods to be the same. That this is true may be seen by consulting the values of  $\alpha$  for 0.075, 0.10, and 0.25 normal in table 52. Owing to slight hydration, the amounts of dissociation, as measured by the freezing-point method, are slightly higher than those measured by the conductivity method. The curves for barium nitrate are given in figs. 24 and 25.

## HYDRATES OF BARIUM BROMIDE AND BARIUM IODIDE.

Since the two barium salts studied are so slightly soluble, it was thought best to add the tables for the hydrates of barium bromide and barium iodide which were prepared by Jones and Bassett<sup>1</sup> (table 53). Both of these salts crystallize with two molecules of water of crystallization.

TABLE 53.—*Hydrates of Barium Bromide and Barium Iodide.*

Hydrates of barium bromide.							Hydrates of barium iodide.						
<i>m</i>	<i>a</i>	<i>L</i>	$\Delta/m$	<i>L'</i>	<i>M</i>	<i>H</i>	<i>m</i>	<i>a</i>	<i>L</i>	$\Delta/m$	<i>L'</i>	<i>M</i>	<i>H</i>
0.10	79.3	4.81	5.06	5.04	2.54	25.4	0.076	78.6	4.78	4.92	4.91	1.47	19.3
0.15	77.7	4.75	4.91	4.88	1.48	9.9	0.153	75.9	4.68	5.00	4.96	3.14	20.5
0.25	73.8	4.60	5.00	4.96	4.03	16.1	0.306	74.9	4.65	5.17	5.08	4.70	15.4
0.40	71.3	4.52	5.09	5.03	5.63	14.1	0.612	71.0	4.54	6.08	5.86	12.51	20.4
0.50	68.8	4.42	5.18	5.09	6.32	12.5	0.917	64.8	4.27	6.69	6.29	17.84	19.5
0.6774	65.3	4.29	5.74	5.59	12.92	19.1	1.222	61.1	4.13	7.54	6.98	22.70	18.1
0.9032	64.8	4.27	5.87	5.66	13.64	15.1	1.528	55.5	3.92	8.67	7.83	27.74	18.2
1.1290	61.1	4.13	6.24	5.93	16.88	14.9	1.834	51.1	3.76	9.54	8.44	31.92	17.4
1.3548	58.4	4.03	6.66	6.28	19.90	14.7	2.139	45.0	3.53	11.22	9.67	35.28	16.5
1.5806	55.6	3.93	7.12	6.63	22.66	14.3							
1.884	50.9	3.75	7.67	7.06	26.05	14.4							
2.258	41.1	3.39	8.34	7.58	30.71	13.6							

The solubilities of these two salts are nearly equal to those of the other halides of the calcium group. It is very probable, owing to the fact that Jones and Bassett used a thermometer less sensitive than the one employed in this work, that the observed freezing-point lowerings for the most dilute solutions are too low. This would, of necessity, give low values for the total combined water and for the hydration.

The values of *M* for these salts increases regularly with increase in concentration. The magnitude of hydration for each salt is approximately constant. If we compare the values of *H* for the four barium salts in tables 48, 52, and 53 we see that, of the halides, the iodide has the greatest hydrating power and the chloride the least, while the bromide stands intermediate between the other two. The nitrate has the least hydrating power.

Since the chloride, bromide, and iodide crystallize each with two molecules of water, we should expect the observed molecular lowering to be greater than the calculated. Experimental results confirm this.

## COBALT CHLORIDE.

An approximately 2 normal solution was first made up. A portion of this was diluted to convenient strength and the cobalt determined electrolytically.

Cobalt chloride crystallizes with 6 molecules of water, and, like the other chlorides with the same amount of water of crystallization, has a large hydrating power. The results are just what we should expect (table 54).

It will be noted, first of all, that the freezing-point lowerings for all concentrations are greater than for any of the salts thus far studied, and hence there is a correspond-

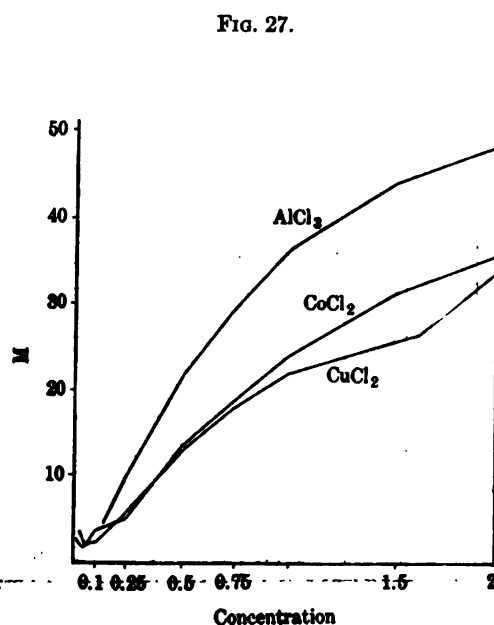
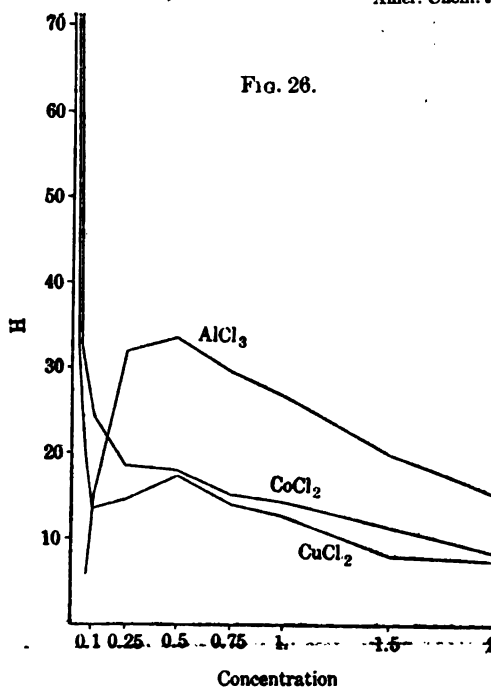
<sup>1</sup>*Loc. cit.*

TABLE 54.—Cobalt Chloride—Data for Freezing-point and Conductivity Measurements, Specific Gravity, and Hydrates.

Freezing-point.					Hydrates.						
<i>m</i>	$\Delta$	$\Delta/m$	<i>i</i>	$\alpha$	<i>m</i>	$\alpha$	<i>L</i>	$\Delta/m$	<i>L'</i>	<i>M</i>	<i>H</i>
0.01	0.06241	6.241	.....	.....	0.025	89.62	5.1938	5.5786	5.5776	3.822	152.88
0.025	0.1394	5.5786	2.9992	99.96	0.05	84.87	5.0717	5.2186	5.2164	2.122	42.44
0.05	0.2609	5.2186	2.8057	90.28	0.075	82.05	4.9122	5.1413	5.1385	2.444	33.68
0.10	0.5110	5.1100	2.7473	87.36	0.10	78.85	4.7932	5.1100	5.1070	3.413	34.13
0.25	1.3040	5.2160	2.8043	.....	0.25	71.61	4.7098	5.2160	5.2057	5.292	28.31
0.50	2.8371	5.6743	3.0507	.....	0.50	63.41	4.2088	5.6743	5.6176	13.93	27.86
0.75	4.5860	6.1147	3.2874	.....	0.75	56.54	3.9632	6.1417	5.9937	18.22	25.09
1.00	6.7157	6.7157	3.6105	.....	1.00	50.92	3.7542	6.7157	6.6394	24.14	24.14
1.5	12.1308	8.0871	4.3532	.....	1.5	41.53	3.4049	8.0871	7.9270	31.69	21.1
2.0	17.7342	8.8671	4.7672	.....	2.0	32.91	3.0842	8.8671	8.6594	35.76	17.88

Conductivity. $\mu_{\infty} 0^\circ = 117$ (Jones and Bassett). <sup>1</sup>			Specific gravity.					
<i>V</i>	$\mu_{\infty}$	$\alpha$	<i>m</i>	Sp. gr.	<i>W</i> <sub>sol</sub>	<i>W</i> <sub>sat</sub>	<i>W</i> <sub>H<sub>2</sub>O</sub>	Correction, per cent.
100	113.06	96.63	0.01	1.00116	1001.159	1.299	999.860	0.014
40	104.86	89.62	0.025	1.00305	1003.052	3.247	999.805	0.019
20	99.30	84.80	0.05	1.00606	1006.065	6.495	999.570	0.043
13.34	96.00	82.05	0.075	1.00919	1009.190	9.742	999.447	0.055
10	92.26	78.85	0.10	1.01239	1012.386	12.990	999.396	0.060
4	83.79	71.61	0.25	1.03049	1030.491	32.475	998.016	0.19
2	73.86	63.14	0.50	1.05492	1054.924	64.95	989.974	1.00
1.334	66.15	56.54	0.75	1.09118	1089.180	97.42	991.655	0.83
1	59.58	50.92	1.00	1.11847	1118.471	129.90	988.571	1.14
0.667	48.59	41.53	1.5	1.17502	1175.026	194.85	980.176	1.98
0.5	38.51	32.91	2.0	1.23637	1236.376	25.98	976.576	2.34

<sup>1</sup>Amer. Chem. Journ., 33, 567 (1905).

ingly greater difference between the observed and calculated lowerings. The amount of water combined with the salt increases regularly from 0.05 normal to the most concentrated solution, as shown by fig. 27. The hydration per molecule decreases rapidly in the most dilute solutions, and approaches a constant value at 0.25 normal. For the curve for hydrates, see fig. 26.

#### COBALT NITRATE.

Cobalt nitrate, like cobalt chloride, crystallizes with 6 molecules of water, and we should expect it to have hydrating power of the same order of magnitude. The data given in table 55 show that such is the case. What has been said regarding cobalt chloride applies equally well to the nitrate.

The curves for the values of  $H$  and  $M$  are found in figs. 28 and 29, respectively.

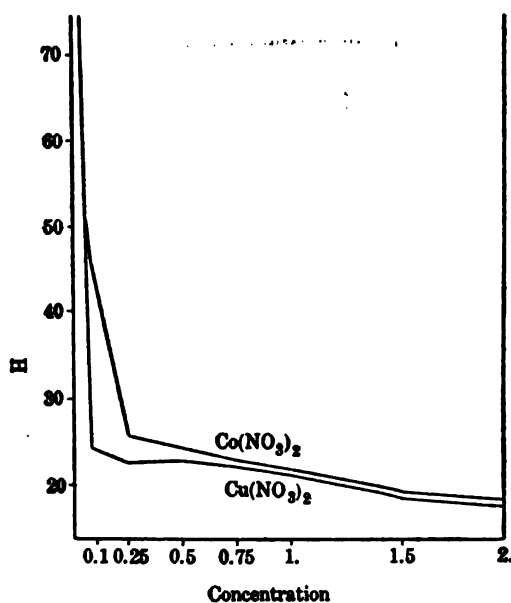


FIG. 28.

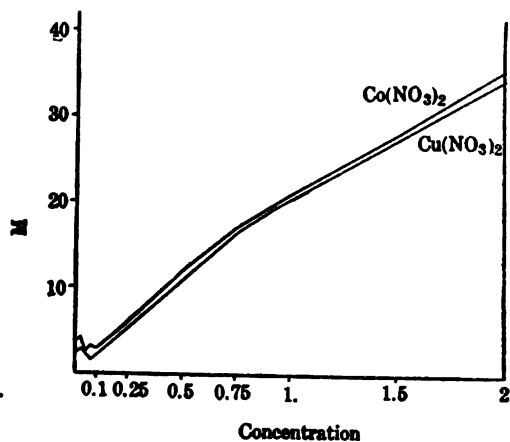


FIG. 29.

TABLE 55.—Cobalt Nitrate—Data for Freezing-point and Conductivity Measurements, Specific Gravity, and Hydrates.

Freezing-point.					Hydrates.						
$m$	$\Delta$	$\Delta/m$	$\mu_0$	$\alpha$	$m$	$\alpha$	$L$	$\Delta/m$	$L'$	$M$	$H$
0.10	0.0553	5.5300	2.9731	98.65	0.025	85.62	5.0451	5.3640	5.3602	3.266	130.6
0.025	0.1341	5.3640	2.8731	93.65	0.05	81.73	4.9003	5.1434	5.1354	2.544	50.8
0.05	0.2572	5.1434	2.7652	88.26	0.075	77.95	4.7597	5.0826	5.0702	3.402	45.3
0.075	0.3812	5.0826	2.7218	86.09	0.10	76.48	4.7050	5.0050	4.9889	3.161	31.6
0.10	0.5005	5.0050	2.7096	85.48	0.25	69.28	4.437	5.082	5.0296	6.445	25.8
0.25	1.2705	5.0082	2.7323	.....	0.5	62.02	4.167	5.417	5.323	12.070	24.1
0.50	2.708	5.417	2.9125	.....	0.75	55.84	3.928	5.784	5.627	16.880	22.5
0.75	4.338	5.784	3.1099	.....	1.00	50.08	3.723	6.220	5.990	21.020	21.0
1.00	6.220	6.220	3.3441	.....	1.5	40.45	3.364	7.192	6.779	27.980	18.7
1.5	10.888	7.192	3.8668	.....	2.0	31.55	3.033	9.431	8.607	30.123	18.0
2.0	18.863	9.431	5.0701	.....							

TABLE 55—Continued.

Conductivity. $\mu_{\infty} 0^{\circ}=117.6$ .			Specific gravity.					
V	$\mu_s$	$\alpha$	m	Sp. gr.	$W_{sol}$	$W_{salt}$	$W_{H_2O}$	Correction, per cent.
100	108.66	92.40	0.01	1.00150	1001.496	1.830	999.652	0.033
40	100.69	85.62	0.025	1.00386	1003.863	4.577	999.286	0.071
20	96.12	81.73	0.05	1.00758	1007.579	9.154	998.425	0.157
13.334	91.67	77.95	0.075	1.01129	1011.289	13.731	997.558	0.244
10	89.94	76.48	0.10	1.01808	1015.084	18.308	996.776	0.322
4	81.48	69.28	0.25	1.03737	1037.37	45.77	991.603	0.83
2	72.94	62.02	0.50	1.07415	1074.15	91.54	982.61	1.73
1.333	65.32	55.54	0.75	1.11204	1110.04	137.31	972.73	2.72
1	58.89	50.08	1.00	1.14612	1146.12	183.08	963.04	3.69
0.668	47.57	40.55	1.5	1.21720	1217.20	274.62	942.58	5.74
0.5	37.10	31.55	2.0	1.28576	1285.76	366.16	919.60	8.04

## COPPER CHLORIDE.

Diluted portions of the mother-solution were taken and the copper in them determined electrolytically.

While copper chloride crystallizes with two molecules of water, its power to combine with water is of the same order of magnitude as that of cobalt chloride and cobalt nitrate, as may be seen in the curves, figs. 26 and 28, and in table 56.

TABLE 56.—Copper Chloride—Data for Freezing-point and Conductivity Measurements, Specific Gravity, and Hydrates.

Freezing-point.					Hydrates.						
m	$\Delta$	$\Delta/m$	i	$\alpha$	m	$\alpha$	L	$\Delta/m$	L	M	H
0.01	0.05703	5.7030	.....	.....	.....	.....	.....	.....	.....	.....	.....
0.05	0.24944	4.9888	2.6821	84.10	0.05	79.98	4.8352	4.9888	4.9871	1.693	33.85
0.075	0.37075	4.9433	2.6576	80.82	0.075	77.72	4.7511	4.9433	4.9392	2.116	28.21
0.100	0.48665	4.8665	2.6164	.....	0.10	75.17	4.6563	4.8665	4.8695	2.354	23.54
0.25	1.2237	4.894	2.6316	.....	0.20	66.83	4.3460	4.8949	4.8821	6.091	24.36
0.50	2.669	5.338	2.8701	.....	0.50	57.56	4.0012	5.3384	5.3076	13.67	27.34
0.75	4.245	5.661	3.0436	.....	0.75	50.86	3.7519	5.6611	5.5748	18.17	24.22
1.00	5.994	5.994	3.2228	.....	1.00	45.00	3.5340	5.9945	5.9088	22.33	22.33
1.50	10.105	6.737	3.6220	.....	1.50	34.84	3.1560	6.7370	6.5747	26.66	17.78
2.0	15.204	7.647	4.1112	.....	2.00	26.30	2.8383	7.6470	7.3836	34.20	17.10

Conductivity. $\mu_{\infty} 0^{\circ}=120$ (Jones and Bassett).			Specific gravity.					
V	$\mu_s$	$\alpha$	m	Sp. gr.	$W_{sol}$	$W_{salt}$	$W_{H_2O}$	Correction, per cent.
100	110.55	92.12	0.01	1.00121	1001.208	1.345	999.863	0.013
20	95.88	79.98	0.05	1.00637	1006.370	6.725	999.645	0.035
13.34	93.27	77.72	0.075	1.00926	1009.264	10.0875	999.176	0.084
10	90.21	75.17	0.10	1.01261	1012.614	13.450	999.164	0.263
4	80.20	66.83	0.20	1.03099	1030.991	33.625	997.366	0.263
2	69.08	57.56	0.50	1.05148	1061.479	67.25	994.229	0.57
1.334	61.03	50.86	0.75	1.09091	1090.91	100.87	990.037	0.99
1	54.01	45.00	1.00	1.12025	1120.24	134.5	985.749	1.42
0.6666	41.81	34.84	1.50	1.17761	1177.61	201.75	975.868	2.41
.05	31.56	26.30	2.0	1.23455	1234.55	269.0	965.55	3.44



The total amount of water combined with the electrolyte passes through a minimum at about 0.05 normal and then increases rapidly with increase in concentration. This is seen in fig. 27, page 71.

## COPPER NITRATE.

The mother-solution of the salt was diluted to convenient strength and the copper determined electrolytically.

TABLE 57.—*Copper Nitrate—Data for Freezing-point and Conductivity Measurements, Specific Gravity, and Hydrates.*

Freezing-point.					Hydrates.						
<i>m</i>	$\Delta$	$\Delta/m$	<i>i</i>	$\alpha$	<i>m</i>	$\alpha$	<i>L</i>	$\Delta/m$	<i>L'</i>	<i>M</i>	<i>H</i>
0.01	0.05736	5.7365	3.0841	.....	.....	.....	.....	.....	.....	.....	.....
0.025	0.13852	5.5401	2.9785	98.92	0.025	75.76	5.0502	5.5401	5.5368	4.8821	195.2
0.05	0.25540	5.1081	2.7463	87.31	0.075	81.10	4.8769	5.1081	5.1005	2.435	48.7
0.075	0.36979	4.9306	2.6508	82.54	0.075	77.85	4.7560	4.9306	4.9188	1.839	24.5
0.25	1.221	4.885	2.6264	81.32	0.25	67.29	4.363	4.885	4.852	5.607	22.4
0.50	2.589	5.178	2.7841	.....	0.50	59.15	4.060	5.178	5.092	11.26	22.5
0.75	4.190	5.587	3.0039	.....	0.75	52.54	3.814	5.587	5.441	16.612	22.15
0.935	5.512	5.895	3.1696	.....	0.935	48.21	3.653	5.895	5.708	19.953	21.3
1.50	10.284	6.856	3.6861	.....	1.50	37.29	3.247	6.856	6.447	27.575	18.38
2.0	16.89	8.44	4.5419	.....	2.0	28.36	2.914	8.440	7.749	24.651	17.32

Conductivity. $\mu_{\infty} 0^{\circ} = 118.1$			Specific gravity.					
<i>V</i>	$\mu_0$	$\alpha$	<i>m</i>	Sp. gr.	<i>W</i> <sub>sol</sub>	<i>W</i> <sub>salt</sub>	<i>W</i> <sub>H<sub>2</sub>O</sub>	Correction, per cent.
100	108.84	92.24	0.01	1.00151	1001.5049	1.876	999.628	0.03
40	101.2	85.76	0.025	1.00408	1004.0764	4.692	999.384	0.06
20	95.7	81.10	0.05	1.00786	1007.8599	9.384	998.4759	0.15
13.34	91.86	77.85	0.075	1.01171	1011.7155	14.076	997.6395	0.23
4	79.4	57.29	0.25	1.04029	1040.2903	46.920	993.370	0.66
.....	69.8	.....	0.50	1.07723	1077.230	93.840	983.390	1.66
1.334	62.0	52.54	0.75	1.11469	1114.699	140.76	973.930	2.60
1.0695	56.89	48.21	0.935	1.14262	1142.627	174.48	968.140	3.18
0.0667	44.0	37.29	1.5	1.22618	1226.183	281.52	944.660	5.53
0.5	33.47	28.36	2.0	1.29262	1292.623	375.36	917.260	8.27

<sup>1</sup>Amer. Chem Journ., 33, 578 (1905).

Copper nitrate crystallizes with 6 molecules of water and, therefore, should give us hydration of the same order of magnitude as that found for the nitrate of cobalt and nickel, which crystallize with the same amount of water. Reference to table 57 will show that this is the fact. The minimum for the total amount of combined water is pronounced and lies between 0.075 and 0.25 normal. The hydration per molecule decreases rapidly with increase in concentration to 0.05 normal, and then becomes approximately constant. The curves representing the values of *H* and *M* are given in figs. 28 and 29, respectively.

## NICKEL NITRATE.

The nickel was determined electrolytically in diluted portions of the mother-solution.

The hydrating power of nickel nitrate is of the same order of magnitude as that of cobalt and copper nitrates, which crystallize with the same amounts of water

(see fig. 30). The total combined water passes through a minimum at 0.05 normal and then increases rapidly with increasing concentration (see fig. 31 and table 58).

TABLE 58.—*Nickel Nitrate—Data for Freezing-point and Conductivity Measurements, Specific Gravity, and Hydrates.*

Freezing-point.					Hydrates.						
<i>m</i>	$\Delta$	$\Delta/m$	<i>i</i>	<i>a</i>	<i>m</i>	<i>a</i>	<i>L</i>	$\Delta/m$	<i>L'</i>	<i>M</i>	<i>H</i>
0.01	0.0550	5.5070	2.9607	98.03	.....	.....	.....	.....	.....	.....	.....
0.025	0.1299	5.1960	2.7950	89.75	0.05	79.83	4.8296	4.9745	4.9679	1.545	30.9
0.05	0.2487	4.9745	2.6744	83.72	0.075	76.0	4.7084	4.8854	4.8749	1.797	25.3
0.075	0.3654	4.8854	2.6265	81.32	0.075	76.57	4.7084	4.8854	4.8749	1.897	25.3
0.10	0.4960	4.9602	2.6667	.....	0.10	74.94	4.6477	4.9675	4.8721	2.560	25.6
0.25	1.251	5.003	2.6901	.....	0.25	68.31	4.041	5.0036	4.9670	6.329	25.3
0.5	2.652	5.305	2.8524	.....	0.50	60.95	4.127	5.305	5.225	11.672	23.3
0.75	4.213	5.618	3.0205	.....	0.75	54.65	3.894	5.618	5.484	16.102	21.4
1.00	6.101	6.101	4.2801	.....	1.00	48.95	3.700	6.102	5.875	20.561	20.5
1.5	10.576	7.051	3.7910	.....	1.5	39.06	3.313	7.051	6.679	27.998	18.6
2.0	17.050	8.523	4.5334	.....	2.0	30.38	2.990	8.525	7.921	34.580	17.3

Conductivity. $\mu_{\infty} 0^{\circ}=117.2.^1$			Specific gravity.					
<i>V</i>	$\mu_s$	<i>a</i>	<i>m</i>	Sp. gr.	<i>W</i> <sub>sol</sub>	<i>W</i> <sub>salt</sub>	<i>W</i> <sub>H<sub>2</sub>O</sub>	Correction, per cent.
100	106.77	91.10	0.01	1.00152	1001.521	1.8278	999.693	0.030
40	100.31	85.58	0.025	1.00388	1003.882	4.5695	999.312	0.068
20	93.57	79.83	0.05	1.00779	1007.792	9.1390	998.653	0.134
13.34	89.74	76.77	0.075	1.01154	1011.541	13.7085	997.029	0.216
10	87.84	74.94	0.10	1.01531	1015.377	18.278	997.029	0.291
4	80.07	68.31	0.25	1.03837	1038.37	45.695	992.68	0.732
2	71.44	60.95	0.5	1.07611	1076.11	91.390	984.72	1.527
1.334	64.06	54.65	0.75	1.11310	1113.10	137.08	976.01	2.39
1.0	57.38	48.95	1.0	1.14562	1145.62	182.78	962.88	3.71
0.667	45.79	39.6	1.5	1.22134	1221.34	274.17	947.17	5.28
0.5	35.61	30.38	2.0	1.29459	1294.59	365.56	929.03	7.09

<sup>1</sup>Amer. Chem. Journ., 33, 574 (1905).

Before going farther it will be interesting to note the great similarity between the salts of cobalt, copper, and nickel which we have just studied. Solutions of the same concentrations were used in all five salts.

Reference to figs. 27, 29, and 31, will show at a glance the close relation between the amounts of water held in combination by these salts, whether they are chlorides or nitrates. We are not surprised at this, since, with the exception of copper chloride, all crystallize with 6 molecules of water. In fact, we found it impossible to put more than two curves on one sheet, so closely did the values agree. From the minimum in the most concentrated solutions studied, the magnitude of the hydrating power is a linear function of the concentration. In other words, each hydrate has its own definite composition, which varies with every concentration.

The curves representing the hydration per molecule (figs. 26, 28, and 30) show the same striking similarity. They are almost asymptotic with the two coordinates. The hydration per molecule decreases very rapidly, for the very dilute solutions, to approximately the same concentration, when they become nearly constant for further increase in concentration.

Two conclusions are to be drawn from these relations. It will be noted that the molecular hydration and the total amount of water held in combination are the same for any two salts containing a common cation. It seems most probable that if the two anions,  $\text{Cl}$  and  $\text{NO}_3$ , possessed very different hydrating power, this influence would manifest itself. It is a well-known fact that organic acids possess little or no hydrating power, and in the work which we have done upon the strong acids—hydrochloric, nitric, and sulphuric—this has been found to hold in the dilute solutions, where the dissociation is practically complete.

This would lead us to conclude that *the hydrating power of any salt is primarily a function of the cation.*

In the discussion of the nitrates and chlorides of the alkaline-earth group, attention was called to the fact that the hydrating power of those salts is an inverse function of the atomic volumes.

In the case of the salts of cobalt, copper, and nickel which we have studied, we have to do with cations which have approximately the same atomic

volumes. As stated by Ostwald, the migration velocity of an organic acid decreases with increase in the mass of the anion, as well as with increase in the mass of the cation in case of the organic bases. We should expect, then, to obtain larger values for conductivity than those given by the alkaline earth metals. Experiment shows the opposite to be the fact. We are, therefore, forced to believe that

the effect of the atomic volume of the ions upon the conductivity is more than compensated for by the relatively large volume of the ionic complex.

Bredig<sup>1</sup> pointed out the fact that the migration velocities of elementary cations are a periodic function of the atomic weights. When plotted in a curve, where the ordinates represent velocities and the abscissas the atomic weights, it will be seen that the alkali metals lie very near the maxima of the curve, along with the halogens. At the extreme minima we find aluminium and chromium. Slightly above these lie the metals of the copper group, zinc, and cadmium, while still higher are to be found the metals of the alkaline earths.

The significance of this periodic relation between the migration velocities of the cations and the atomic weights has never been satisfactorily explained.

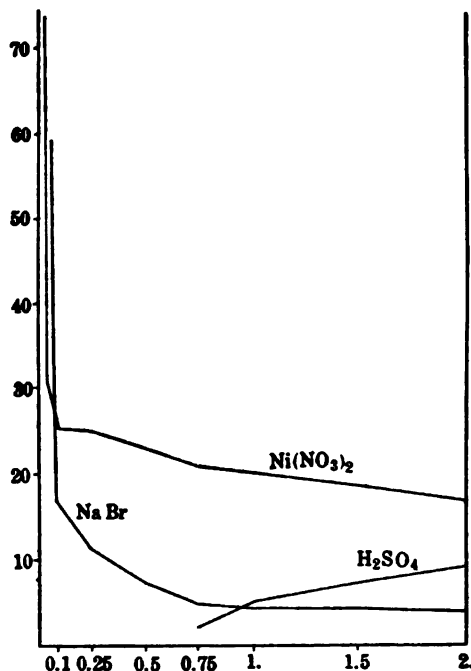


FIG. 30.

<sup>1</sup>Zeit. phys. Chem., 33, 242 (1894).

We believe that we have found the cause of this phenomenon. Of two ions or ionic complexes of different volumes, that one will meet with less friction on moving through the solution which has the smaller volume. Consequently, it will have the greater velocity. On the other hand, the greater the volume, the greater will be the friction to be overcome by the ion, and, hence, the smaller the velocity. Therefore we should expect to find that those salts which crystallize with little or no water of crystallization give greater values for conductivity than those crystallizing with a greater amount.

It is a well-known law that the conductivity of an electrolyte depends upon the velocities of the ions. These velocities, in turn, depend upon the fluidity and the volume of the ion. The greater the volume, the greater will be the resistance offered to the movement of the ions.

If we consider the alkalis we find that potassium, rubidium, and cesium, which have the largest atomic volumes and whose salts generally crystallize without water, have the greatest migration velocities, while lithium and sodium, which have smaller atomic volumes and whose salts crystallize with 2 or 3 molecules of water, have very much smaller migration velocities.

Comparing the members of the calcium group, we find that the atomic volumes increase with increasing atomic weight. The migration velocities of the cations calcium and strontium, whose salts usually crystallize with 6 molecules of water, are approximately equal to that of the barium cation, whose salts crystallize either with 2 molecules of water or water-free. On the other hand, the magnesium cation, of smaller atomic volume, has a slightly smaller migration velocity, due to the more complex composition of its hydrates.

The cations of cobalt, copper, and nickel have approximately the same atomic weights, the same atomic volume, and the same hydrating power. Since these cations have the greatest hydrating power of any which we have studied, we should expect them to have the smallest migration velocities, and such is the case.

#### ALUMINIUM CHLORIDE.

Special interest is attached to the study of aluminium chloride, owing to the fact that it is a quaternary electrolyte and crystallizes with 6 molecules of water.

The hydrolytic effect of water upon this salt, in dilute solutions, can be noted in the first two concentrations. The hydrochloric acid liberated is almost completely dissociated at the dilutions in question, thus giving values for  $C$  which are considerably higher than would be obtained if the salt were not hydrolyzed. This may be attributed to one or both of two causes: the very high migration velocity of the hydrogen ion or its inability to form hydrates. It is at about 0.075 normal that the influence due to the hydration of the aluminium cation begins to predominate. Just as we should expect, the number of molecules of water held in combination by one molecule of the electrolyte is large and increases very rapidly with increase in concentration (see fig. 27). In the curve representing the hydration per molecule (fig. 26), that part representing concentrations between 0.075 and 0.5 normal represents the abnormality in the hydration due to hydrolysis.

A glance at column *a* (table 59) shows us that, in spite of the tendency of this salt to hydrolyze, the dissociation decreases very rapidly with increase in concentration. This is just what might be predicted. Its atomic volume is very small and the hydrating power of its cation very large; therefore it should have a very small migration velocity.

TABLE 59.—Aluminium Chloride—Data for Freezing-point and Conductivity Measurements, Specific Gravity, and Hydrates.

Freezing-point.					Hydrates.						
<i>m</i>	$\Delta$	$\Delta/m$	<i>i</i>	<i>a</i>	<i>m</i>	<i>a</i>	<i>L</i>	$\Delta/m$	<i>L'</i>	<i>M</i>	<i>H</i>
0.01	0.712	7.1200	3.8279	94.26	0.01	92.04	6.9958	7.1200	7.1180	.....	.....
0.025	0.1623	6.4940	3.4193	80.64	0.025	83.08	6.4958	6.4940	6.4907	.....	.....
0.050	0.3053	6.1060	3.2827	76.09	0.050	76.72	6.1409	6.1060	6.1012	.....	.....
0.075	0.4511	6.0153	3.2340	74.46	0.075	74.50	6.0111	6.1526	6.1447	.....	.....
0.10	0.4511	5.0850	3.2704	.....	0.10	71.80	5.8664	6.1560	6.1452	2.52	25.2
0.25	1.6604	6.641	3.5708	.....	0.25	62.88	5.368	6.641	6.613	10.54	42.16
0.50	3.9446	7.889	4.2415	.....	0.50	44.12	4.321	9.511	9.362	9.91	39.88
0.75	7.1339	9.511	5.1137	.....	.....	.....	.....	.....	.....	.....	.....
1.00	11.795	11.795	6.3410	.....	1.00	36.42	3.892	11.795	11.523	36.78	36.78
1.50	25.5 <sup>1</sup>	17.000	9.1398	.....	1.5	24.48	3.225	17.000	16.369	44.60	29.33
2.0	48.5 <sup>1</sup>	24.25	13.037	.....	2.0	14.98	2.695	24.25	22.963	49.03	24.51

Conductivity. $\mu_{\infty} 0^{\circ} = 170.^2$			Specific gravity.					
<i>V</i>	$\mu_s$	<i>a</i>	<i>m</i>	Sp. gr.	<i>W</i> <sub>sol</sub>	<i>W</i> <sub>salt</sub>	<i>W</i> <sub>H<sub>2</sub>O</sub>	Correction, per cent.
100	156.48	92.04	0.01	1.00104	1001.04	1.3345	999.71	0.029
40	141.24	83.08	0.025	1.00282	1002.82	3.3625	999.49	0.051
20	130.44	76.72	0.05	1.00588	1005.88	6.6725	999.21	0.079
13.334	126.66	74.50	0.075	1.00870	1008.70	10.0067	998.70	0.130
10	122.07	71.80	0.1	1.01158	1011.58	13.345	998.24	0.176
4	106.90	62.88	0.25	1.02911	1029.11	33.36	995.75	0.425
2	88.60	52.11	0.55	1.05706	1057.06	66.725	990.33	0.966
1.333	75.02	44.12	.....	1.08431	1084.31	100.067	988.22	1.57
1	61.93	36.42	1.00	1.11054	1110.54	133.45	977.09	2.29
1.6667	41.62	24.48	1.5	1.16308	1163.08	200.175	962.90	3.70
0.5	25.47	14.98	2.00	1.21378	1213.78	266.90	946.88	5.31

<sup>1</sup>These freezing-points were determined by an alcohol thermometer, and freezing-mixtures of solid carbon dioxide and ether.

<sup>2</sup>Amer. Chem. Journ., 31, 333 (1904).

#### SODIUM BROMIDE.

Dilute portions of the mother-solution were standardized volumetrically by Volhard's method. This salt differs from those preceding in that it is a binary electrolyte and crystallizes with two molecules of water. A study of table 60 brings out the same general results. The observed molecular lowering passes through a minimum between 0.5 and 0.75 normal. The minimum in the total amount of combined water occurs at 0.10 normal. From the amounts of water which combine with one gram-molecule of the salt, it will be seen that the sodium cation has nearly the same hydrating power in dilute solutions as do the cations of the calcium and copper groups.

The atomic volume of sodium is slightly more than half that of potassium. Its hydrating power, however, for the more dilute solutions is much greater. If, then, the amount of hydration of the sodium ion is more than sufficient to compensate for

the inverse volume relations, we should expect the migration velocity of sodium to be less than that of potassium. This has been found to be the case.

The atomic volume of sodium is also slightly less than that of calcium, and considerably less than those of strontium and barium; yet, owing to the greater hydration of the cations of the calcium group, its migration velocity is greater.

For the curves representing the values of  $H$  and  $M$ , see figs. 30 and 31.

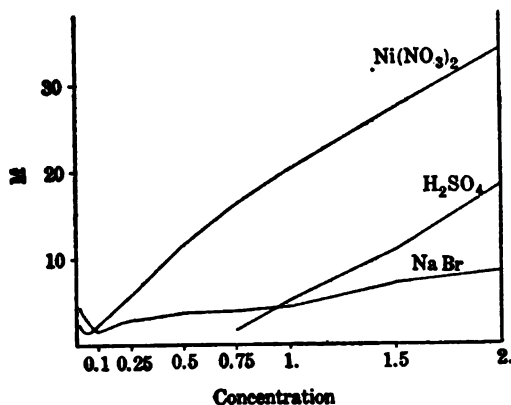


FIG. 31.

TABLE 60.—Sodium Bromide—Data for Freezing-point and Conductivity Measurements, Specific Gravity, and Hydrates.

Freezing-point.					Hydrates.						
<i>m</i>	$\Delta$	$\Delta/m$	<i>i</i>	$\alpha$	<i>m</i>	$\alpha$	<i>L</i>	$\Delta/m$	<i>L'</i>	<i>M</i>	<i>H</i>
0.01	0.03936	3.9360	.....	.....	0.025	91.53	3.5624	3.8050	3.8075	3.575	143.0
0.025	0.0952	3.8090	2.0478	104.78	0.05	89.44	3.5235	3.7260	3.7221	2.963	59.2
0.05	0.1863	3.7260	2.0032	100.32	0.075	87.36	3.4848	3.636	3.6297	2.217	24.29
0.075	0.2727	3.636	1.9548	95.48	0.10	85.73	3.4545	3.572	3.5635	1.700	17.00
0.10	0.3572	3.572	1.9204	92.04	0.25	79.21	3.333	3.543	3.521	2.974	11.39
0.25	0.885	3.543	1.9049	90.49	0.50	76.78	3.288	3.574	3.529	3.803	7.60
0.50	1.787	3.574	1.9215	.....	0.75	76.08	3.275	3.595	3.526	3.961	5.28
0.75	2.696	3.595	1.9327	.....	1.00	72.83	3.233	3.536	3.536	4.763	4.76
1.00	3.633	3.633	1.9481	.....	1.5	70.56	3.172	3.769	3.637	7.103	4.73
1.5	5.654	3.769	2.0263	.....	2.00	66.22	3.101	3.873	3.665	8.547	4.27
2.00	7.746	3.873	2.0822	.....							

Conductivity. $\mu_{\infty}0^{\circ}=64.48.^1$			Specific gravity.					
<i>V</i>	$\mu$	$\alpha$	<i>m</i>	Sp. gr.	<i>W</i> <sub>sol</sub>	<i>W</i> <sub>salt</sub>	<i>W</i> <sub>H<sub>2</sub>O</sub>	Correction, per cent.
100	61.12	94.78	0.01	1.00073	1000.732	1.030	999.700	0.030
40	59.02	91.53	0.025	1.00218	1002.177	2.575	999.602	0.040
20	57.67	89.44	0.05	1.00407	1004.074	5.150	998.924	0.107
13.334	56.33	87.36	0.075	1.00597	1005.972	7.725	998.247	0.175
10	55.28	85.73	0.10	1.00788	1007.88	10.30	997.58	0.24
4	51.08	79.21	0.25	1.01964	1019.64	25.75	993.89	0.26
2	49.51	76.78	0.50	1.03908	1039.08	51.50	987.58	1.24
1.333	49.06	76.08	0.75	1.05811	1058.11	77.25	980.86	1.91
1	47.61	73.83	1.00	1.07632	1076.32	103.01	973.31	2.66
0.6667	45.50	70.56	1.50	1.11963	1119.63	154.51	965.12	3.48
0.5	42.70	66.22	2.00	1.15240	1152.40	206.02	946.38	5.36

<sup>1</sup>Amer. Chem. Journ., 34, 375 (1905).

## HYDROCHLORIC ACID.

Having investigated fifteen salts, attention was next turned to the study of some of the more common acids.

An approximately 3 normal solution of hydrochloric acid was prepared. Dilute portions of the mother-solution were then titrated against a standard solution of potassium hydroxide free from carbonate. This, in turn, had been standardized by means of a 0.1 normal solution of freshly prepared oxalic acid. The results are given in table 61.

TABLE 61.—*Hydrochloric Acid—Data for Freezing-point and Conductivity Measurements, Specific Gravity, and Hydrates.*

Freezing-point.					Hydrates.						
<i>m</i>	$\Delta$	$\Delta/m$	<i>i</i>	$\alpha$	<i>m</i>	$\alpha$	<i>L</i>	$\Delta/m$	<i>L'</i>	<i>M</i>	<i>H</i>
0.025	0.0902	3.6080	1.9377	93.97	0.025	98.75	3.6967	3.6080	3.6060	.....	.....
0.05	0.1799	3.5980	1.9344	93.44	0.05	98.18	3.6861	3.5980	3.5960	.....	.....
0.075	0.2681	3.5752	1.9221	92.21	0.075	97.87	3.6803	3.5752	3.5702	.....	.....
0.10	0.3567	3.5670	1.9177	91.77	0.10	96.40	3.6547	3.5670	3.5610	.....	.....
0.25	0.8862	3.5450	1.9059	90.59	0.25	93.77	3.6041	3.5450	3.5280	.....	.....
0.50	1.841	3.682	1.9794	.....	0.20	.....	3.5021	3.5310	3.6260	1.58	3.16
0.75	2.852	3.804	2.0450	.....	0.75	85.80	3.455	3.803	3.747	3.33	5.77
1.00	3.975	3.975	2.1372	.....	1.00	84.35	3.428	3.975	3.899	6.707	6.70
1.50	6.452	4.301	2.3123	.....	1.5	76.73	3.287	4.301	4.176	11.820	7.88
2.00	9.367	4.683	2.5177	.....	2.0	70.93	3.179	4.683	4.502	16.32	8.16

Conductivity. $\mu_{\infty} 0^{\circ}=236.92$ .			Specific gravity.					
<i>V</i>	$\mu$	$\alpha$	<i>m</i>	Sp. gr.	<i>W</i> <sub>sol</sub>	<i>W</i> <sub>sat</sub>	<i>W</i> <sub>H<sub>2</sub>O</sub>	Correction, per cent.
40	233.95	98.75	0.025	1.00034	1000.34	0.911	999.429	0.057
20	232.60	98.18	0.05	1.00101	1001.01	1.822	999.188	0.081
13.33	231.87	97.87	0.075	1.00135	1001.35	2.734	998.616	0.138
10	228.61	96.49	0.10	1.00180	1001.80	3.645	998.155	0.184
4	222.17	93.77	0.25	1.00425	1004.25	9.114	999.136	0.486
2	211.79	89.39	0.50	1.00849	1008.49	18.229	990.261	0.973
1.333	203.28	85.80	0.75	1.01264	1012.64	27.343	985.297	1.470
1	199.85	84.35	1.00	1.01749	1017.49	36.458	981.032	1.896
0.667	181.79	76.73	1.5	1.02542	1025.42	54.687	970.733	2.92
0.5	168.04	70.93	2.0	1.03414	1034.14	72.916	961.224	3.87

A glance at table 61 shows that, for the more dilute solutions, the corrected observed freezing-point lowering (*L'*) is less than that calculated from the dissociation. This is due to one of two causes—the very high migration velocity of the hydrogen ion or its inability to form hydrates.

The minimum in the freezing-point lowering occurs at about 0.25 normal. For dilutions greater than 0.5 normal, there is no evidence of hydration. At 0.5 normal, however, the hygroscopic property of the molecular hydrochloric acid begins to predominate over the effect of decrease in dissociation. From this point the amount of combined water increases with increase in concentration. The corresponding values of *H* differ from those of the other electrolytes thus far studied in that they, also, increase as the concentration increases.

The values of *H* and *M*, for hydrochloric acid, are plotted in figs. 22 and 23, p. 62.

## NITRIC ACID.

A moderately concentrated solution was first made up, care having been taken that the acid used contained none of the oxides of nitrogen in solution.

Dilute portions of this were standardized volumetrically against a solution of potassium hydroxide.

TABLE 62.—*Nitric Acid—Data for Freezing-point and Conductivity Measurements, Specific Gravity, and Hydrates.*

Freezing-point.					Hydrates.						
<i>m</i>	$\Delta$	$\Delta/m$	<i>i</i>	$\alpha$	<i>m</i>	$\alpha$	<i>L</i>	$\Delta/m$	<i>L'</i>	<i>M</i>	<i>H</i>
0.025	0.09035	3.6140	1.9430	94.30	0.025	99.08	3.7028	3.6140	3.6124	.....	.....
0.05	0.1791	3.5830	1.9263	92.63	0.05	98.65	3.6948	3.5830	3.5790	.....	.....
0.075	0.2678	3.5713	1.9200	92.00	0.075	96.87	3.6617	3.5713	3.5640	.....	.....
0.10	0.3547	3.5470	1.9069	90.69	0.10	95.43	3.6348	3.5470	3.5370	.....	.....
0.25	0.8869	3.4576	1.9073	90.73	0.25	93.99	3.6062	3.5476	3.5210	.....	.....
0.50	1.798	3.597	1.9341	.....	0.5	91.38	3.559	3.597	3.544	.....	.....
0.75	2.766	3.681	1.9736	.....	0.75	89.17	3.518	3.680	3.595	1.180	1.57
1.00	3.749	3.749	2.0156	.....	1.00	85.93	3.450	3.749	3.639	2.880	2.88
1.5	5.955	3.970	2.1344	.....	.....	.....	.....	.....	.....	.....	.....
2.0	8.383	4.191	2.2532	.....	2.00	74.71	3.249	4.191	3.944	9.78	4.89

Conductivity. $\mu_{\infty} 0^{\circ}=237.07$ .			Specific gravity.					
<i>V</i>	$\mu_s$	$\alpha$	<i>m</i>	Sp. gr.	<i>W</i> <sub>sol</sub>	<i>W</i> <sub>sat</sub>	<i>W</i> <sub>H<sub>2</sub>O</sub>	Correction, per cent.
40	234.89	99.08	0.025	1.00093	1000.926	1.576	999.35	0.065
20	233.88	98.65	0.05	1.00180	1001.798	3.152	998.64	0.134
13.33	229.66	96.87	0.075	1.00265	1002.653	4.728	997.92	0.207
10	226.24	95.43	0.10	1.00350	1003.496	6.304	997.19	0.281
4	222.82	93.99	0.25	1.00848	1008.48	15.762	992.71	0.728
2	216.63	91.38	0.50	1.01686	1016.86	31.524	985.34	1.465
1.334	211.43	89.17	0.75	1.02503	1025.03	48.280	978.75	2.325
1.0	203.72	85.93	1.00	1.03360	1033.60	63.050	970.55	2.945
0.5	177.15	74.71	2.00	1.06700	1067.00	126.090	940.91	5.909

Like hydrochloric acid, dilute solutions of nitric acid exhibit no tendency to form hydrates. No appreciable power to combine with water is manifested until the concentration 0.75 normal is reached. The amount of total combined water, then, increases with the concentration. The same results are obtained for the values of *H*. For curves representing the values of *H* and *M* see figs. 24 and 25, page 66. The data are given in table 62.

## SULPHURIC ACID.

Dilute portions of the mother-solution were titrated against the standard potassium hydroxide used for the previous acids.

The results are given in table 63, the curves in figs. 30 and 31.

In dilute solutions no water is held in combination. The total amount of water held in combination by the acid, and the hydration per molecule, increase with concentration from 0.75 to 2 normal.



A comparison of figs. 22, 24, and 30 shows that the hydrating powers of hydrochloric and sulphuric acids are of approximately the same order of magnitude, while that of nitric acid is slightly less.

Figs. 23, 25, and 31, representing the total amounts of combined water for the three acids, show that the same relation holds here as for the hydrates.

TABLE 63.—*Sulphuric Acid—Data for Freezing-point and Conductivity Measurements, Specific Gravity, and Hydrates.*

Freezing-point.					Hydrates.						
<i>m</i>	$\Delta$	$\Delta/m$	<i>i</i>	$\alpha$	<i>m</i>	$\alpha$	<i>L</i>	$\Delta/m$	<i>L'</i>	<i>M</i>	<i>H</i>
0.01	0.04872	4.8720	2.6193	80.96	0.01	82.06	4.9126	4.8720	4.8708	.....	.....
0.025	0.1179	4.7184	2.6357	76.84	0.025	72.80	4.5681	4.7184	4.7159	.....	.....
0.050	0.2182	4.3640	2.3462	67.31	0.05	69.13	4.4316	4.3640	4.3582	.....	.....
0.075	0.3157	4.2099	2.2634	63.17	0.075	66.63	4.3386	4.2099	4.2007	.....	.....
0.10	0.4043	4.0434	2.1738	58.69	0.10	64.78	4.2698	4.0434	4.0312	.....	.....
0.25	0.9865	3.9460	2.1215	56.07	0.25	61.04	4.1306	3.9460	3.9132	.....	.....
0.50	2.0033	4.0066	2.1541	.....	0.5	57.99	4.017	4.266	3.939	.....	.....
0.75	3.1174	4.156	2.2346	.....	0.75	55.88	3.938	4.156	4.048	1.512	2.00
1.00	4.379	4.379	2.3544	.....	1.0	53.37	3.845	4.379	4.226	5.004	5.00
1.50	7.265	4.843	2.6042	.....	1.5	48.28	3.656	4.844	4.585	11.257	7.50
2.00	11.296	5.648	3.0365	.....	2.0	43.11	3.464	5.648	5.236	18.801	9.40

Conductivity. $\mu_{\infty} 0^\circ = 485.42$ .			Specific gravity.					
<i>V</i>	$\mu_s$	$\alpha$	<i>m</i>	Sp. gr.	<i>W</i> <sub>tot</sub>	<i>W</i> <sub>sol</sub>	<i>W</i> <sub>H<sub>2</sub>O</sub>	Correction, per cent.
100	398.34	82.06	0.01	1.00072	1000.719	0.980	999.74	0.026
40	353.41	72.80	0.025	1.00190	1001.91	2.451	999.45	0.054
20	335.56	69.13	0.05	1.00355	1003.55	4.902	998.65	0.135
13.34	323.43	66.63	0.075	1.00515	1005.15	7.353	997.79	0.220
10	314.42	64.78	0.1	1.00677	1006.77	9.807	996.97	0.303
4	296.30	61.04	0.25	1.01618	1016.18	24.51	991.67	0.832
2	281.53	57.99	0.5	1.03218	1032.18	49.03	983.14	1.68
1.384	271.25	55.88	0.75	1.04760	1047.60	73.53	974.07	2.59
1.00	259.05	53.37	1.00	1.06307	1063.07	98.07	964.99	3.50
0.6667	234.38	48.28	1.5	1.09345	1093.45	147.11	946.34	5.36
0.5	209.28	43.11	2.0	1.12316	1123.51	196.15	926.99	7.30

#### DISCUSSION.

Fifteen salts and three strong acids have been studied in this investigation. We have worked with solutions covering a range of concentration from 0.01 to 3.0 normal; at one extremity are found to predominate, in a very pronounced manner, those influences due to the ions; at the other, those due to the molecules also manifest themselves. In this way we have attempted to compare the relative effects of the ions and the molecules upon the molecular lowering of the freezing-point and the dissociation.

Comparing, first of all, the freezing-point lowerings for any given solution, it is found that, without exception, the molecular lowering calculated from the dissociation decreases regularly with increasing concentration. Naturally, this follows from the fact that the decrease in dissociation is regular throughout. On the other hand, the corrected observed freezing-point lowering decreases very rapidly in the dilute

solutions, passes through a very pronounced minimum, and then increases as the concentration increases. A glance at the tables of the hydrates shows that in every case the observed molecular lowering produced by any salt is greater than the calculated lowering based on conductivity measurements.

If there were no hydration, we should expect the observed and the calculated molecular lowerings to be equal, except for the difference due to the influence of the friction between the ion and the solvent. The nearest approach to this condition which we have met is found in the most concentrated solutions of barium nitrate. Here the observed molecular lowering is about 1 per cent greater than the calculated value. An equally satisfactory agreement was found by Jones and Stine for solutions of potassium chloride, which, likewise, crystallizes without water.

The values of  $M$  and  $H$  also show that the abnormality of the freezing-point lowering in the dilute solutions is greatly augmented by the relatively great hydrating power of the ions.

Since, then, the hydration of the ion increases with increase in dilution, the volume and mass of the ionic complex are greater the more dilute the solution, and, therefore, the greater will be the resistance to be overcome by the ion as it moves through the solvent. This being the case, the dissociation as measured by the conductivity method will be *less* than the true dissociation, and the abnormality in the dissociation measured will increase with increasing dilution.

The effect produced by adding more of the given electrolyte will be to break down these larger hydrates into simpler ones with smaller volume, thus decreasing the resistance to the motion of the hydrated ion.

This agrees well with the results of Jones and Uhler.<sup>1</sup> They found that the number of ether waves of different wave-length with which a given particle will vibrate in resonance, decreases with increasing dilution, thereby producing a narrowing of the absorption bands. On the other hand, the addition of more of the same electrolyte, or a strong dehydrating agent, decreases the complexity of the hydrate, thereby decreasing its period. As a result, the particles are free to vibrate in resonance with a greater number of wave-lengths, and the absorption bands widen.

It will be seen that, with the exception of magnesium chloride, the value of  $M$ , the total amount of water held in combination by one molecule of the electrolyte, decreases rapidly in the dilute solutions, passes through a minimum, and then becomes a linear function of the concentration.

The hydration per molecule decreases rapidly to approximately the same concentration which corresponds to a minimum in the freezing-point lowering, and then remains practically constant as the concentration increases. Eliminating the hydration due to the ions, the hydration per molecule in solution over a given range of temperature is constant, just as the amount of water with which that same salt will crystallize from solution is constant for a given range of temperature. This relation is best illustrated by the curves representing the values of  $H$ . They are almost asymptotic to the coordinates.

Having found that the ions of a salt are hydrated, the next question which arises is this: Is it the cation or the anion which has the greater hydrating power?

<sup>1</sup>Amer. Chem. Journ., 27, 126 (1907); Carnegie Institution of Washington Publication No. 60.

Nernst, Garrard, and Oppermann,<sup>1</sup> in a study of the concentration changes which take place in an indifferent substance during electrolysis, have calculated that the ions  $\text{SO}_4$ ,  $\text{Cl}$ ,  $\text{Br}$ , and  $\text{NO}_3$  drag with them 9, 5, 4, and 2.5 molecules of water, respectively.

It is seen from a study of the chlorides and nitrates of the copper group, each of which crystallizes with 6 molecules of water (copper chloride alone separating with two molecules), that the hydration per molecule is approximately the same for all of these salts. If, as Nernst and his coworkers have found, the hydrating power of the  $\text{NO}_3$  ion is only one-half that of the  $\text{Cl}$  ion, then we should expect the influence of the hydrating power of these two anions to manifest itself in the hydrating power of the salts in question, and especially so since the three cations are so nearly alike chemically. On the basis of this reasoning we are forced to conclude that the *hydrating power of any salt is primarily a function of the cation.*

We do not deny that the anions are capable of forming hydrates; but, if they do, experiments lead us to believe that they have this power only to a relatively slight degree.

We have noted also this striking relation. It is well known that if the atomic volumes of the elements are plotted as ordinates against the atomic weights as abscissæ, there exists between them a periodic relation. At the maxima of the curve are the alkali metals. The three elements having the largest atomic volumes are potassium, rubidium, and cæsium. Salts of these metals usually crystallize from aqueous solution in the anhydrous form, and, as experiments have shown, they have very slight hydrating power in solution. Lithium and sodium, some of whose salts crystallize with 2 and 3 molecules of water, have much smaller atomic volumes.

At the minimum of the third section of the atomic-weight curve we find the elements strontium, iron, cobalt, copper, and nickel. The salts of these metals crystallize with large amounts of water, and show great hydrating power in solution. Aluminium, which has less than half the atomic weight of iron, but slightly greater atomic volume, lies at the second minimum. Its salts crystallize with 8 and 9 molecules of water and show great hydrating power in solution.

Comparing the metals of the alkaline-earth group we find that barium, whose salts crystallize with 2 molecules of water or water-free, has the largest atomic volume. The other members of this group form salts which crystallize with 6 molecules, calcium nitrate excepted. The magnesium cation, which has the smallest atomic volume, has the greatest hydrating power in solution; the strontium cation, which has the largest atomic volume, has a smaller hydrating power than does the calcium cation, whose atomic volume is slightly less.

This is conclusive evidence that the *hydrating power of the cation is an inverse function of its atomic volume.*

That the velocities of the ions are an inverse function of their mass (and perhaps of their volumes) is an established fact. Experimental evidence, however, seems at variance with this statement. We should expect those ions which have the smallest atomic volumes to have the greatest migration velocities. On the contrary,

<sup>1</sup>Göttingen Nachr., 1900, p. 86.

we find that potassium, rubidium, and caesium have the greatest migration velocities ( $\text{H}^+$  and  $\text{OH}^-$  excepted), while the ions of the iron and copper groups, with very small atomic volumes, have the smallest migration velocities.

A glance at the two curves representing the relation between atomic volume and atomic weights, and between migration velocities and atomic weights, shows at once the cause of this apparent anomaly. It has been found that those elements which have the smallest atomic volumes have the greatest hydrating power, and *vice versa*. We see, then, that *those ions which have the smallest migration velocities have also the greatest hydrating power*.

A somewhat detailed comparison of the members of the different groups will bring out this idea more clearly.

The atomic volumes of potassium, rubidium, and caesium increase rapidly with increasing atomic weights; and, as a rule, their salts crystallize without water. We should expect, then, the potassium ion to have the greatest migration velocity and the caesium ion to have the smallest. Experiments show that they have approximately the same migration velocities. Sodium and lithium, whose atomic volumes are less than half that of potassium, have migration velocities which are only about two-thirds that of potassium. It will be remembered that sodium and lithium form salts which may crystallize with 2 and 3 molecules of water, respectively. Hence, we may assume that the increase in volume of the sodium and lithium ions, due to the formation of a relatively large hydrate, decreases the velocity of those ions to a far greater extent than the slight hydration of the large potassium ion decreases the velocity of that ion.

The atomic volume of lithium is about one-half that of sodium, and the maximum amount of water with which lithium salts crystallize from solution is 3 molecules, whereas the maximum for sodium salts is 2 molecules. Since the ratio of 2:3 represents approximately the ratio of the hydrating power of the two ions in solution, we should expect the effect upon the velocity of the greater increase in the volume of the small lithium ion, due to its hydration, to compensate somewhat for the smaller increase in the volume of the larger sodium ion. Experiment shows that the migration velocities are nearly equal.

The same relation holds for the metals of the alkaline-earth group. The atomic volumes increase with increasing atomic weight. The migration velocities of the cations calcium and strontium, whose salts crystallize with 6 molecules of water, are approximately equal to that of the barium cation, whose salts crystallize either with 2 molecules of water or water-free. On the other hand, the magnesium cation, which has one-half the atomic volume of the calcium ion, has nearly the same migration velocity, due to compensation between the atomic volumes and the hydration of the ions.

The calcium ion has a slightly greater atomic volume than sodium, yet, owing to its much greater hydrating power, its migration velocity is considerably less.

The cations copper, cobalt, and nickel have nearly the same atomic volumes and the same hydrating power. We should expect them to have the same migration velocity, and such is the case.

The atomic volumes of the halogens chlorine, bromine and iodine, are approximately the same. If their ions are hydrated we should expect them to combine with the same amounts of water, and, therefore, they should have migration velocities of the same order of magnitude. This has been found to be the case. The atomic volume of fluorine has not been determined, but from its position on the migration-velocity curve we should infer that its atomic volume is smaller than that of the halogens, and that its ion possesses a considerable degree of hydrating power.

Further, it will be noted that the migration velocities of the halogens are almost identical with those of the alkalis standing next above them in order of atomic weights, whereas their atomic volumes are very much smaller. This leads us to believe that the compensation, which brings about an equalization of the migration velocities of the two groups, is due to the increase in volume of the alkali ions by hydration.

The silver ion alone, of all the metallic elements for which satisfactory data can be found, presents an exception. It has a small atomic volume, and its salts crystallize from solution without water. We should expect it to have but slight hydrating power in solution, and it should, therefore, have a high migration velocity, but this has been found to be slightly less than that of the halogens.

According to the law of Raoult, the lowering of the freezing-point of a given weight of solvent by a dissolved substance is directly proportional to the amount of the substance dissolved, providing that substance is a non-electrolyte. In the case of electrolytes the lowering produced by gram-molecular weights of the dissolved substances are greater than those produced by gram-molecular weights of non-electrolytes. This abnormality in the case of electrolytes is explained by the fact that an ion and a molecule lower the freezing-point to the same extent.

The fact is that the freezing-point method gives us a relation between the amount of solvent acting as such and the number of dissolved particles, whether they are molecules or ions.

Having determined the freezing-point lowering for any concentration of a given electrolyte, it is an easy matter to calculate the amount of dissociation. For binary electrolytes  $\alpha$  is obtained from the expression  $\alpha = i - 1$ , where  $i$  is the van't Hoff  $i$ .

For ternary electrolytes,  $\alpha = \frac{i-1}{2}$ , and for quaternary electrolytes  $\alpha = \frac{i-1}{3}$ .

We have calculated the values of  $\alpha$  from the molecular lowerings of all the solutions studied, for the dilute solutions up to the concentration at which the molecular lowering passes through a minimum. Beyond this concentration the molecular lowering of the freezing-point increases, due to hydration, and, consequently, the calculated dissociation would increase. For that reason the values of  $\alpha$  have not been calculated.

In the case of every salt studied, without exception, *the dissociation as calculated from the freezing-point lowering is higher than the dissociation as calculated from the conductivity measurements.*

This will be seen by comparing the values obtained for  $\alpha$  in the tables representing the freezing-point and conductivity measurements for each salt.

If there were no hydration these values should be equal. Since the freezing-point measurements give us the most accurate relation between the amount of the actual solvent and the number of dissolved particles, it, therefore, must give us the most accurate measure of the dissociation, when hydration is taken into account.

The conductivity of a solution is, as we have seen, dependent upon the number of ions present, their velocity, their mass and volume, and the viscosity of the solution. Since the temperatures at which the dilute solutions freeze are approximately only one-fourth of a degree or less below the freezing-point of pure water—the temperature at which the conductivity measurements were made—we must conclude that the number of ions present and their velocities are in the two cases the same. Similarly, the viscosity of the solutions is the same in both measurements, and, therefore, the friction between solvent and ion will vary directly as the surface of the latter.

We have shown that most metallic ions in solution have great hydrating power, and that the degree of hydration varies inversely with the atomic volume of the ion. The ions which have the greatest hydrating power are those which have the smallest atomic volumes, and should, therefore, if there were no hydration, meet with less friction in their movements through the solution. They should have greater migration velocities, while exactly the opposite results are found.

A comparison of the values of  $\alpha$  for a dilute solution of the strong acids shows that the dissociation as measured by conductivity is greater in every case than the dissociation measured by the freezing-point method. In the more concentrated solutions the observed freezing-point lowerings are higher than the molecular lowerings calculated from conductivity. This is due to the fact that the molecules or ions of those acids have considerable hydrating power, and we obtain in concentrated solutions results of the same character as with the salts.

#### SUMMARY.

1. The freezing-point lowerings and the conductivities of solutions of a number of electrolytes, over a wide range of concentration, have been carefully redetermined.
2. We observe that the molecular lowerings of the freezing-point of all the electrolytes studied pass through a very pronounced minimum at concentrations ranging from 0.1 to 0.25 normal. The molecular lowerings calculated from the dissociation, as measured by conductivity, decrease regularly from the most dilute to the most concentrated solutions.
3. The magnitude of the molecular lowerings produced by molecular quantities of different salts varies directly as the number of molecules of water with which those salts crystallize from solution. The magnitude of the hydrating power of salts in solution is, in turn, proportional to the amount of water of crystallization.
4. That the ions have very great hydrating power is shown by the values of  $M$  and  $H$  for the different salts. The total amount of combined water decreases with increase in concentration, passes through a minimum, and then increases regularly with increase in concentration. The amount of water held in combination by one molecule of a salt is very large in the more dilute solutions where the ions predominate. It decreases rapidly with decrease in dissociation, and approaches a constant value at greater concentration.

5. The hydrating power of a salt is, primarily, a function of the cation. The results show that two salts which crystallize with the same amounts of water of crystallization and contain a common cation exhibit hydrating power of the same order of magnitude.

6. It has been found that the hydrating power of a cation is an inverse function of its atomic volume. Those cations which have the smallest atomic volumes have the greatest hydrating power, and *vice versa*. We may state the relations thus: *The hydrating power of the ions is a function of their atomic weights.*

7. Furthermore, we have found that those cations which have the greatest migration velocities exhibit, also, the smallest hydrating power, and *vice versa*. This probably accounts for the apparent anomaly which exists in the relation between the migration velocities of the ions and their atomic weights and atomic volumes. The influence upon the migration velocity of the hydration of those ions with small atomic volumes is greater than that of the small hydration of those ions which have large atomic volumes.

8. In the case of every salt it has been found that the dissociation in the dilute solutions, as measured by the conductivity method, is *less* than that calculated from the freezing-point lowering. Since the freezing-point and conductivity measurements of the dilute solutions were made at approximately the same temperature, the number of the ions present, their velocities, and their hydration are practically the same in both cases. The solutions have, likewise, the same viscosity. Therefore, the friction between the solvent and ion will vary directly as the surface of the latter. This being the case, the greater the dilution the greater will be the complexity of the hydrate, and, consequently, its surface. We should expect to find, therefore, a greater abnormality in the dissociation, as measured by the two methods, the greater the dilution at which the measurements are made. The results show this to be the fact.

It is only in case of those salts which crystallize in the anhydrous condition that we obtain comparable values for the dissociation as measured by the two methods. These values are found only in those concentrations which lie close to that concentration which gives the minimum molecular lowering.

## WORK OF H. R. KREIDER.

### EXPERIMENTAL.

This investigation was undertaken for the purpose of obtaining facts by means of which the following questions might be answered:

1. At what dilutions do the maxima in conductivity occur for various salts in methyl and ethyl alcohols?
2. Is there any relation between these maxima in conductivity for different salts in different solvents?
3. What is the magnitude of the dissociation of these salts in these solvents as calculated by means of the maxima in conductivity?
4. What relation does this dissociation bear to that found by means of the boiling-point method?

### APPARATUS.

The Kohlrausch method was used. The wire was calibrated and was found to be of uniform thickness throughout.

The cells were of the latest type used in this laboratory. They were devised for measuring the conductivity of very dilute solutions where there is great resistance. They consist of two concentric platinum cylinders so placed one within the other that the electrodes are only about 1 mm. apart. (See fig. 32.) They are held together by means of small drops of fusion glass placed between them. These electrodes have a surface of about 48.75 square cm. One of these cells had a constant as low as 2.82. The vertical position of the electrodes permitted the ready escape of all air bubbles, neither were they difficult to wash and dry if the proper precautions were observed. These cells gave excellent results, and a sharp minimum was obtained upon the bridge without difficulty. The constants were determined by means of 0.01 N and 0.001 N solutions of potassium chloride. These constants were frequently redetermined, but were found to change but little throughout the work.

All the apparatus was carefully calibrated. The necessary precautions concerning temperature were observed. The temperature in the 25° bath was determined with a sensitive thermometer calibrated against a German Reichsanstalt thermometer. The 0° bath was from time to time tested to see that there was no change in temperature. At no time were measurements made when the temperature varied more than 0.04° from that required. Careful tests were made to find the time required for the temperature of the solutions within the cells, both at 0° and 25°, to reach an

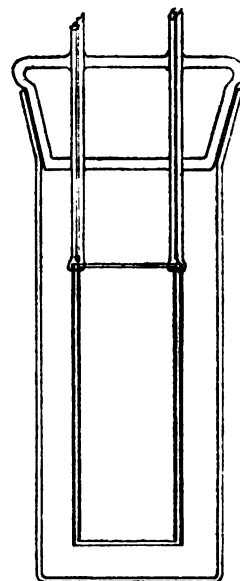


FIG. 32.—Type of cell employed in this work.



equilibrium. This equilibrium was indicated by a constant conductivity. In all cases nearly an hour was necessary. Three readings were always made and the mean was taken.

For 0° measurements a battery jar filled with ice and water was placed within a bucket and surrounded with ice and water. The cells were placed in the battery jar and covered with glass. Ample time was allowed for the temperature to reach equilibrium. Frequently the first reading was repeated after an interval of fifteen minutes or more, insuring equilibrium.

Extreme precautions were necessary in washing the apparatus. No fumes were permitted in the room. Immediately before using, the cells and flasks were thoroughly washed with distilled water, then rinsed several times with conductivity water, and finally washed repeatedly with alcohol. This alcohol was always kept pure and used only a few times before it was dried and redistilled. Ether was not employed in drying, since there is danger of fats being contained in it. The apparatus was then carefully dried. Before a solution was made up in a flask the latter was rinsed with a portion of the solvent, and the cell was rinsed with a portion of the solution. In many cases of very dilute solutions the flask in which the solution was to be made up was first cleaned, dried and rinsed with alcohol, the conductivity of this alcohol determined, and this same alcohol was employed to dilute the solution and its conductivity was used for the correction for the specific conductivity of the solvent. As a rule there was little change in this conductivity when the above precautions were observed, and yet, because of the large volume, this change was at times quite appreciable.

#### SALTS.

The salts used were potassium iodide, ammonium bromide, potassium sulphocyanate, lithium nitrate, sodium iodide, copper chloride, calcium nitrate, and cobalt chloride.

In all cases the necessary precautions were observed in purifying the salts, Kahlbaum's best products being employed. All were recrystallized a number of times finally from conductivity water and some from absolute alcohol. All were dried at a temperature of 125° to 150°. Those which are very deliquescent were heated for a long time, some for several days in an air-bath. Those chlorides which readily form oxychlorides when heated in the air were recrystallized several times, then dried in a vacuum desiccator over sulphuric acid for several days, and finally heated for a long time in a current of dry hydrochloric acid gas. They were then placed in a desiccator over sulphuric acid and potassium hydroxide for several days. All other salts except the latter class were dried to constant weight before making up each solution.

#### SOLVENTS.

The solvents used were methyl and ethyl alcohols and mixtures of these with water. Considerable difficulty was experienced in purifying methyl alcohol so as to obtain it with as low a specific conductivity as possible. This low conductivity was important, since there was danger of introducing considerable error due to the large correction for the specific conductivity of the solvent at these high dilutions. It was evident from the results that some foreign substance was contained in the methyl

alcohol which it was difficult to remove. It was supposed that this unusually high conductivity was due probably to pyridine bases, and that these might be removed by treatment with sulphuric acid. The cold alcohol was treated with a small quantity of dilute sulphuric acid. It was then distilled, the first runnings being always discarded, and the receiver removed while a considerable quantity was still in the flask. The alcohol was then boiled with lime for a day and distilled. In some cases it was repeatedly treated with lime and repeatedly distilled. One quantity thus treated gave a conductivity as low as  $7.1 \times 10^{-7}$ . On standing, however, the conductivity changed somewhat, so that not all work was done with alcohol having quite such low conductivity.

The ethyl alcohol was distilled from lime several times, then repeatedly distilled until it had a conductivity of about  $2.6 \times 10^{-7}$ . The water was purified by the method of Jones and Mackay.

## SOLUTIONS.

All solutions were made by direct weighing. In those cases where the solutions were to be very dilute and but a small quantity of the salt was needed, a 0.1 N solution was made as a mother-solution. This was then diluted to a second mother-solution. From this the final dilutions were made directly. Only in a few cases was a final dilution made from any other except the first or the second mother-solution.

All solutions were made up at 20°. Enough time was always allowed for the temperature to come to equilibrium. The solutions when once placed in the cells were not removed from them until after measurements were made for both temperatures. They were never left in the cells longer than necessary, because of possible decomposition.

TABLE 64.—*Conductivity of Certain Solutions at 0° and 25°.*

Solution.	In methyl alcohol.				In ethyl alcohol.			
	V	0°	25°	Temperature coefficients.	V	0°	25°	Temperature coefficients.
Potassium iodide.....	1,024	69.05	96.18	0.01572	1,024	23.4	36.4	0.02222
	2,048	70.62	99.22	0.01620	2,048	28.6	44.9	0.02280
	4,096	71.48	101.14	0.01660	4,096	29.4	47.2	0.02422
	8,192	72.13	102.4	0.01679	8,192	32.7	47.5	0.01810
	16,384	74.5	104.8	0.01627	16,384	32.5	47.4	0.01834
	32,768	66.6	107.2	0.01598	33,168	32.0	47.2	0.01900
Ammonium bromide.....	1,024	66.1	93.1	0.01634	1,024	32.1	37.0	0.02047
	2,048	69.9	94.1	0.01377	.....	.....	.....	.....
	4,096	70.6	96.7	0.01482	4,096	25.2	39.6	0.02285
	8,129	71.8	96.8	0.01393	16,384	27.5	39.1	0.01687
	16,584	69.2	94.9	0.01485	65,536	29.8	39.5	0.01302
Potassium sulphocyanate..	1,600	69.1	98.3	0.01690	1,600	28.2	43.8	0.02218
	3,200	71.1	101.0	0.01682	3,200	28.6	45.7	0.02391
	.....	.....	.....	.....	6,400	29.2	46.67	0.02393
	12,800	73.0	103.7	0.01682	12,800	29.23	45.4	0.02213
	25,600	83.5	106.3	0.01092	25,600	28.57	43.64	0.02110
Lithium nitrate	1,600	58.83	83.24	0.01659	1,600	23.82	36.67	0.02157
	3,200	59.89	85.98	0.01743	3,200	24.13	38.44	0.02372
	6,400	61.46	89.29	0.01811	6,400	25.63	40.87	0.02378
	12,800	59.69	91.35	0.02121	12,800	25.87	40.02	0.02187
	25,600	60.36	93.61	0.02203	25,600	.....	43.30	.....

TABLE 64—Continued.

Solution.	In methyl alcohol.				In ethyl alcohol.			
	V	0°	25°	Temperature coefficients.	V	0°	25°	Temperature coefficients.
Sodium iodide..	512	60.32	87.67	0.01814	512	24.41	38.06	0.02237
	1,024	64.15	90.91	0.01669	1,024	25.12	39.66	0.02315
	2,048	63.65	91.93	0.01777	2,048	25.89	40.92	0.02322
	4,096	63.34	91.06	0.02382	4,096	26.89	41.84	0.02224
	8,192	65.90	93.40	0.01669	8,192	26.06	42.86	0.02579
	16,384	63.10	91.80	0.01819	16,384	26.79	42.02	0.02274
Calcium nitrate	32,768				32,768	28.83	43.22	0.01996
	1,600	83.53	106.04	0.01078	1,600	17.19	24.48	0.01696
	3,200	93.50	120.58	0.01156	3,200	19.11	29.52	0.02179
	6,400	105.46	138.46	0.01252	6,400	21.45	34.16	0.02370
	12,800	112.52	151.73	0.01394	12,800	24.22	39.23	0.02537
	25,600	119.44	164.6	0.01509	25,600	27.61	45.67	0.02616
Cobalt chloride	51,200	124.58	175.0	0.01620	51,200	31.92	51.62	0.02469
	1,600	101.94	138.58	0.01438	1,600	19.99	25.61	0.01125
	3,200	110.98	152.34	0.01878	3,200	22.75	30.13	0.01278
	6,400	115.76	162.38	0.01612	6,400	25.68	34.15	0.01319
	12,800	116.22	165.74	0.01704	12,800	29.25	39.01	0.01335
	25,600	115.34	166.08	0.01760	25,600	31.36	43.62	0.01564
Copper chloride	51,200	112.58	157.96	0.01614	51,200	31.62	46.31	0.01858
					102,400	28.42	(52.26)	
	1,600	64.13	78.58	0.09013	1,600	16.08	20.96	0.01214
	3,200	75.43	89.31	0.07361	3,200	18.94	25.74	0.01436
	6,400	85.22	101.28	0.07538	6,400	21.06	30.70	0.01831
	12,800	91.3	112.3	0.09201	12,800	22.52	34.16	0.02067
	25,600	90.5	116.4	0.01145	25,600	22.94	37.79	0.02589
	51,200	79.1	112.1	0.01669				

TABLE 65.—Conductivities of Potassium Iodide in Certain Mixtures.

Percentage.	In methyl alcohol and water.				In ethyl alcohol and water.			
	V	0°	25°	Temperature coefficients.	V	0°	25°	Temperature coefficients.
25 per cent. ....	1,024	45.03	90.44	0.04023	1,024	32.38	74.80	0.05241
	2,048	44.26	91.60	0.04278	2,048	32.75	76.23	0.05311
	4,096	45.60	92.80	0.04140	4,096	32.73	76.60	0.05361
	8,192	45.56	92.40	0.04112	8,192	33.88	77.20	0.05115
	16,384	48.60	96.0	0.04000	16,384	35.30	80.3	0.05138
	32,768	51.99	100.7	0.04517	32,768	39.88	86.8	0.04702
50 per cent. ....	1,024	35.77	72.24	0.04078	1,024	20.04	52.12	0.06401
	2,048	36.07	73.37	0.04137	2,048	20.92	52.83	0.06073
	4,096	37.49	74.64	0.03968	4,096	21.28	53.20	0.06000
	8,192	38.04	76.20	0.04013	8,192	21.34	54.09	0.06120
	16,384	40.18	79.9	0.03945	16,384	20.94	55.23	0.06550
	32,768	46.86	93.1	0.03948	32,768	23.10	59.16	0.06244
75 per cent. ....	1,024	41.63	71.37	0.04952	1,024	20.58	44.14	0.04579
	2,048	41.20	72.00	0.05064	2,048	21.39	45.04	0.04423
	4,096	41.82	73.19	0.05247	4,096	21.50	45.91	0.04541
	8,192	44.98	75.41	0.05475	8,192	21.34	45.96	0.04615
	16,384	46.83	75.3	0.05339	16,384	21.85	47.85	0.04760
	32,768	49.95	71.8	0.01910	32,768	23.68	51.04	0.04491
					65,536	25.11	53.30	0.04491

TABLE 66.—*Conductivities of Cobalt Chloride in Certain Mixtures.*

Percentage.	In methyl alcohol and water.				In ethyl alcohol and water.			
	V	0°	25°	Temperature coefficients.	V	0°	25°	Temperature coefficients.
25 per cent.....	1,600	66.85	144.1	0.04620	1,600	47.92	119.7	0.05992
	3,200	68.20	148.5	0.04831	3,200	49.08	123.6	0.06072
	6,400	69.39	151.8	0.04749	6,400	50.80	127.4	0.06032
	12,800	70.50	152.3	0.04641	12,800	50.73	129.7	0.06227
	25,600	72.08	159.0	0.04823	25,600	51.83	135.0	0.06419
	51,200	80.30	181.6	0.05046	51,200	57.74	154.4	0.06697
50 per cent.....	1,600	53.94	113.5	0.04417	1,600	31.16	81.56	0.06469
	3,200	55.84	115.7	0.04287	3,200	32.27	84.67	0.06495
	6,400	56.59	119.4	0.04440	6,400	32.70	86.56	0.06588
	12,800	57.86	122.3	0.04456	12,800	33.70	88.28	0.06479
	25,600	58.70	124.1	0.04457	25,600	33.25	87.42	0.06517
	51,200	65.2	138.6	0.04503	51,200	34.18	90.8	0.07743
75 per cent.....	1,600	56.23	101.5	0.03220	1,600	31.0	67.1	0.04658
	3,200	63.32	115.4	0.03290	3,200	32.4	70.5	0.04704
	6,400	64.22	118.1	0.03356	6,400	33.1	73.4	0.04870
	12,800	66.48	120.7	0.03262	12,800	33.7	74.6	0.04855
	25,600	66.2	122.3	0.03390	25,600	34.4	74.8	0.04698
	51,200	69.00	124.9	0.03241	51,200	34.0	72.4	0.04518

TABLE 67.—*Conductivities of Potassium Iodide in Mixtures of Methyl Alcohol and Water and of Ethyl Alcohol and Water at 0° and 25°.*

Degree.	In methyl alcohol and water.						In ethyl alcohol and water.					
	V	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.	V	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
At 0°..	1,024	87.9	45.0*	35.8	41.6*	69.1	1,024	87.9	32.4	20.0	20.6	23.4
	2,048	88.5	44.3	36.1	41.2	70.6*	2,048	88.5	32.8*	20.9	21.4	28.6
	4,096	88.9	45.6	37.5	41.8	71.5	4,096	88.9	32.7	21.3*	21.5*	29.4
	8,192	89.2*	46.6	38.0*	45.0	72.1	8,192	89.2*	33.9	21.3	21.3	32.7*
	16,384	89.2	46.6	40.2	46.8	74.5	16,384	89.2	35.3	20.9	21.8	32.5
	32,768	89.2	52.0	46.9	49.9	76.6	32,768	89.2	39.9	23.1	23.7	32.0
At 25°.	1,024	135.6	90.4	72.2	71.4	96.2	1,024	135.6	74.1	52.1	44.1	36.4
	2,048	136.2	91.6	73.4	72.0	99.2	2,048	136.2	76.2	52.8	45.0	44.9
	4,096	136.7	92.8*	74.7	73.2	101.1	4,096	136.7*	76.6	53.2	45.9	47.2
	8,192	136.9*	92.4	76.2	75.4*	102.4	8,192	136.9	77.2	54.1	46.0*	47.5
	16,384	136.9	95.3	79.9	75.3	104.8	16,384	136.9	80.3	55.2	47.9	47.4*
	32,768	136.9	100.7	93.1	71.8	107.2	32,768	136.9	86.8	59.2	51.0	47.2

TABLE 68.—*Conductivities of Cobalt Chloride in Mixtures of Methyl Alcohol and Water and of Ethyl Alcohol and Water at 0° and at 25°.*

Degree.	In methyl alcohol and water.					In ethyl alcohol and water.				
	V	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.	V	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
At 0°.....	1,600	66.9	53.9	56.2	101.9	1,600	47.92	31.16	31.0	19.99
	3,200	68.2	55.8	63.3	111.0	3,200	49.08	32.27	32.4	22.75
	6,400	69.4	56.6	64.2	115.8	6,400	50.80*	32.70	33.1	25.68
	12,800	75.5*	57.9	66.5*	116.2*	12,800	50.73	33.70*	33.7	29.25
	25,600	72.1	58.7	66.2	115.3	25,600	51.83	33.25	34.4*	31.36
	51,200	80.3	65.2	69.0	112.6	51,200	57.74	34.18	34.0	31.62*
At 25°.....						162,400	60.20	34.40		28.42
	1,600	144.1	113.5	101.5	138.58	1,600	119.7	81.56	67.1	25.61
	3,200	148.5	115.7	115.4	152.34	3,200	123.6	84.67	70.5	30.13
	6,400	151.8	119.4	118.1	162.38	6,400	127.4	86.56	73.4	34.15
	12,800	152.3	122.3	120.7	165.74	12,800	129.7	88.28	74.6	39.01
	25,600	159.0	124.1	122.3	166.1	25,600	135.0	87.42	74.8	43.62
	51,200	181.6	136.6	124.9	158.0	51,200	154.4	90.8	72.4	46.31

TABLE 69.—*Dissociation of Potassium Iodide and Cobalt Chloride in Certain Mixtures at 0°.*

	V	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
Potassium iodide in methyl alcohol and water at 0°.....	1,024	98.4	100.0	94.2	100.0	97.8
	2,048	99.2		95.0		100.0
	4,096	100.0		98.7		
	8,192			100.0		
Potassium iodide in ethyl alcohol and water at 0°.....	1,024	98.4	98.7	93.9	95.8	71.5
	2,048	99.2	100.0	98.1	99.5	87.4
	4,096	100.0	100.0	100.0	100.0	90.0
	8,192					100.0
Cobalt chloride in methyl alcohol and water at 0°.....	1,600	100.0	88.6		84.5	87.6
	3,200		90.3		95.1	95.5
	6,400		91.9		96.5	99.6
	12,800		100.0		100.0	100.0
Cobalt chloride in ethyl alcohol and water at 0°.....	1,600	100.0	94.2	92.5	93.0	63.2
	3,200		96.6	95.7	94.1	72.0
	6,400		100.0	97.0	96.2	81.2
	12,800			100.0	97.9	92.5
	25,600				100.0	92.2
	51,200					100.0

TABLE 70.—*Maxima in Molecular Conductivity for Certain Salts in Pure Alcohols.*

	In methyl alcohol.		In ethyl alcohol.	
	0°	25°	0°	25°
KI.....	(77.5)	(112.6)	32.7	47.5
NH <sub>4</sub> Br.....	71.8	96.8	(30.3)	39.6
KCNS.....	(69.2)	(110.4)	29.2	46.7
LiNO <sub>3</sub> .....	61.5	(96.7)	25.9	40.8
NaI.....	64.1	91.9	27.0	42.8
CuCl <sub>2</sub> .....	91.3	116.4	(25.7)	(32.7)
Ca(NO <sub>3</sub> ) <sub>2</sub> .....				
CoCl <sub>2</sub> .....	116.2	166.0	31.6	(46.7)

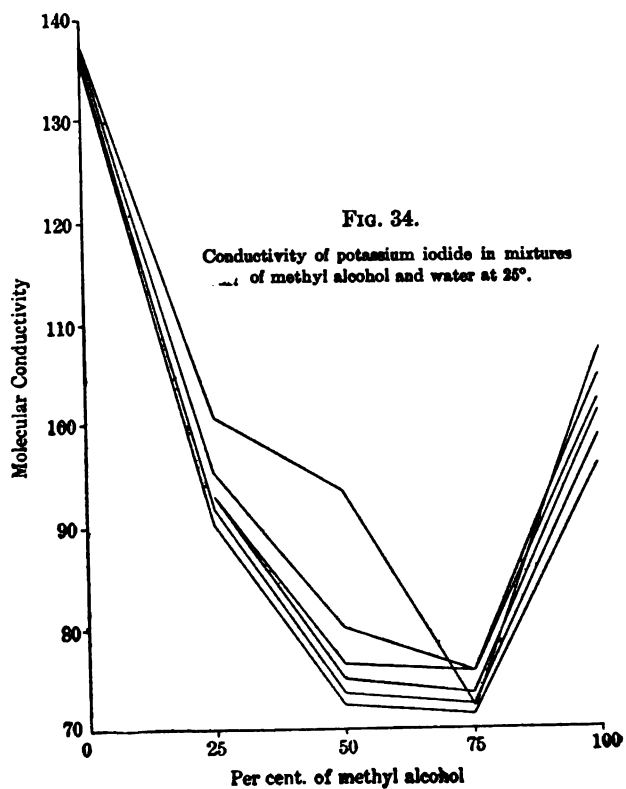
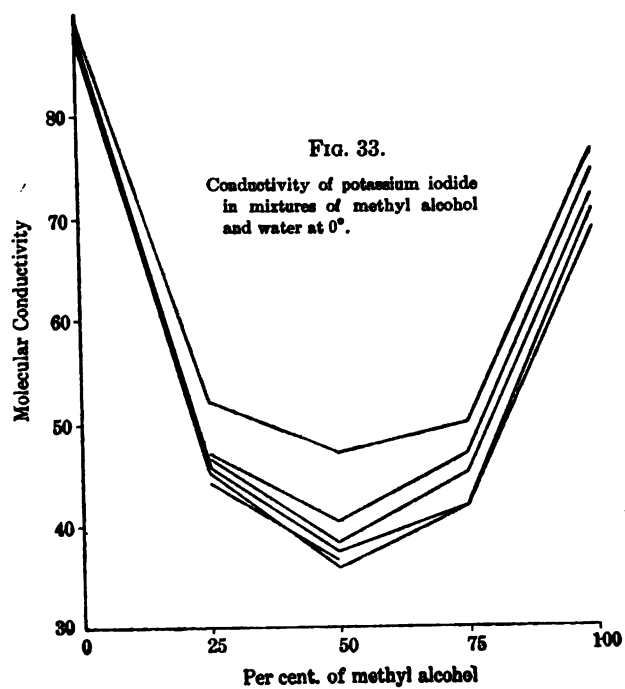
TABLE 71.—*Boiling-point Data.*

	Sol- vent.	Salt.	Concen- tration.	Rise.	Molecular rise.	Dissoc- iation.
Sodium iodide in methyl alcohol...	53.949	2.8131	0.03478	0.429	12.33	46.8
	55.352	2.7357	0.03300	0.425	12.90	53.6
	61.195	2.5597	0.02790	0.356	12.74	51.8
	52.842	2.1082	0.02661	0.347	13.04	55.2
	57.480	2.2060	0.02560	0.318	12.42	47.8
	55.686	1.7227	0.02108	0.263	12.50	48.8
	54.510	1.8380	0.02268	0.298	13.14	56.4
	59.798	1.8080	0.02005	0.251	12.52	49.0
	55.546	1.1943	0.01421	0.178	12.52	49.0
	53.215	0.9665	0.01211	0.155	12.80	52.4
Sodium iodide in ethyl alcohol....	53.100	3.1715	0.03984	0.585	14.63	27.7
	54.734	2.7683	0.03374	0.512	15.17	31.9
	64.744	3.2084	0.03303	0.495	14.98	30.2
	53.896	2.6133	0.03235	0.481	14.87	29.3
	61.293	2.5117	0.02730	0.402	14.73	28.0
	55.509	2.0431	0.02455	0.365	14.86	29.1
	61.701	2.1323	0.02306	0.351	15.22	32.3
	59.294	1.9686	0.02214	0.327	14.76	28.3
	54.368	1.5300	0.01877	0.281	14.97	30.1
	64.926	1.4171	0.01455	0.223	15.32	33.2
Calcium nitrate in methyl alcohol.	56.762	1.4954	0.01685	0.160	9.969	9.5
	64.823	1.2154	0.01142	0.107	9.366	8.6
	52.567	0.9792	0.01135	0.106	9.340	6.8
	63.825	1.2489	0.01131	0.110	9.725	7.9
	62.275	0.7453	0.00729	0.073	10.009	9.3
Calcium nitrate in ethyl alcohol...	50.476	1.1004	0.01328	12.68	0.168	5.1
	54.301	1.3570	0.01228	12.86	1.158	5.9
	52.355	0.6795	0.00791	12.51	0.099	4.4
Cadmium iodide in ethyl alcohol..	48.831	3.5915	0.02007	0.253	12.60	4.8
	54.657	3.6962	0.01850	0.230	12.43	4.0
	50.956	3.1632	0.01694	0.214	12.63	4.9
	51.574	2.9277	0.01549	0.195	12.58	4.7
	52.348	2.7683	0.01443	0.181	12.57	4.6
	52.316	2.6784	0.01397	0.176	12.58	4.6
	48.034	2.1137	0.01201	0.152	12.67	5.0
	51.668	1.2491	0.00660	0.082	12.42	4.0
	56.563	0.8712	0.04204	0.052	12.38	4.3

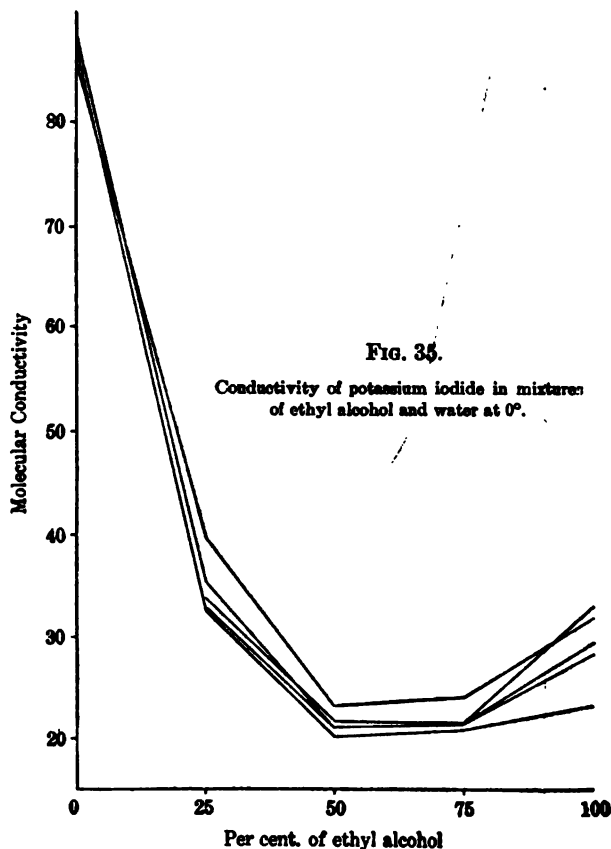
## DISCUSSION OF RESULTS.

Table 64 shows the conductivity of the various salts worked with in the pure solvents at both 0° and 25°. A maximum either at one or both temperatures is frequently shown. Other substances show no maximum up to the highest dilutions measured. In several cases maxima occur at one temperature and none at the other. In some cases the maxima occur at the same concentration at both temperatures, in others at different concentrations, but they always occur at concentrations which are close together. The temperature coefficients in general agree very well. Nearly all show a slight increase with increasing dilution.

Tables 65 and 66 show the conductivity of potassium iodide and cobalt chloride in mixtures of methyl alcohol and water at both 0° and 25°. In some cases the maximum conductivities are reached. The maxima generally occur at a greater concen-



tration at 0° than at 25°. In a few cases the maxima occur at the same concentration at both temperatures. In nearly every case where there is a maximum there is a slight decrease in conductivity, then a rapid increase as dilution increases, thus giving an inflection in the curve.



Figs. 33 to 36 give the curves for the conductivities of potassium iodide in mixtures of methyl alcohol and water and of ethyl alcohol and water. The abscissæ represent the percentage of alcohol and the ordinates the conductivity. In fig. 33 there is a marked minimum with 50 per cent methyl alcohol. Fig. 34 shows a minimum with 75 per cent methyl alcohol. Fig. 35 for potassium iodide in methyl alcohol-water mixtures shows the same characteristics. Fig. 36 shows a minimum for only three concentrations; these are with 75 per cent ethyl alcohol.

Figs. 37 to 40 are the curves for the conductivity of cobalt chloride in methyl alcohol-water mixtures and ethyl alcohol-water mixtures at both 0° and 25°. Fig. 37 shows a minimum with 50 per cent methyl alcohol. Fig. 38 shows minima in the curves with 75 per cent ethyl alcohol. In figs. 39 and 40 there is no minimum.

Tables 67 and 68 represent the values for the conductivities of potassium iodide and cobalt chloride in mixed solvents, arranged according to temperature. The proportions in which the solvents are mixed and the concentrations vary. A study of the maxima of conductivity in these tables is interesting. The more probable values for  $\mu_{\infty}$  are indicated by an asterisk (\*). By means of these values we have calculated



the dissociation of the salts at different volumes for one of these tables (67), since these present more  $\mu_{\infty}$  values than the rest. We have used the well-known equation,  $\alpha = \frac{\mu_0}{\mu_{\infty}}$  and the values for  $\alpha$  are given in table 69. In table 66 no  $\mu_{\infty}$  occurs for 50 per cent methyl alcohol-water mixtures.

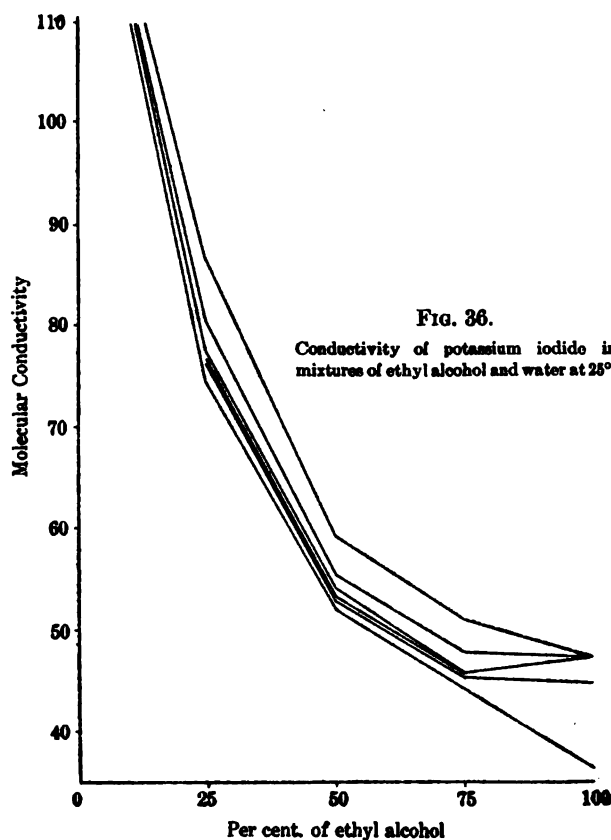


FIG. 36.  
Conductivity of potassium iodide in  
mixtures of ethyl alcohol and water at 25°.

These values for dissociation are interesting when compared with the values for the corresponding molecular conductivities. Fig. 41 gives the curves for dissociation corresponding to the molecular conductivity as indicated by the curves in fig. 35. Fig. 42 in the same manner corresponds to fig. 37 and fig. 43 to fig. 39.

In fig. 35 the conductivity curves of potassium iodide in ethyl alcohol-water mixtures at 0° show minima for all dilutions, while the corresponding curves for dissociation in fig. 41 at first rise. If the equation  $\alpha = \frac{\mu_0}{\mu_{\infty}}$  holds for mixed solvents, this would indicate that at 0° the dissociation in 25 per cent ethyl alcohol-water mixtures is slightly greater than in pure water. In all mixtures the dissociation is very much greater than it is in pure alcohol.

Fig. 42 gives the curves for cobalt chloride in methyl alcohol-water mixtures, corresponding to the molecular conductivity as represented by fig. 37. The curves for dissociation show minima, but the drop below the straight line of averages is very small when compared with the large and decided minima in fig. 37.

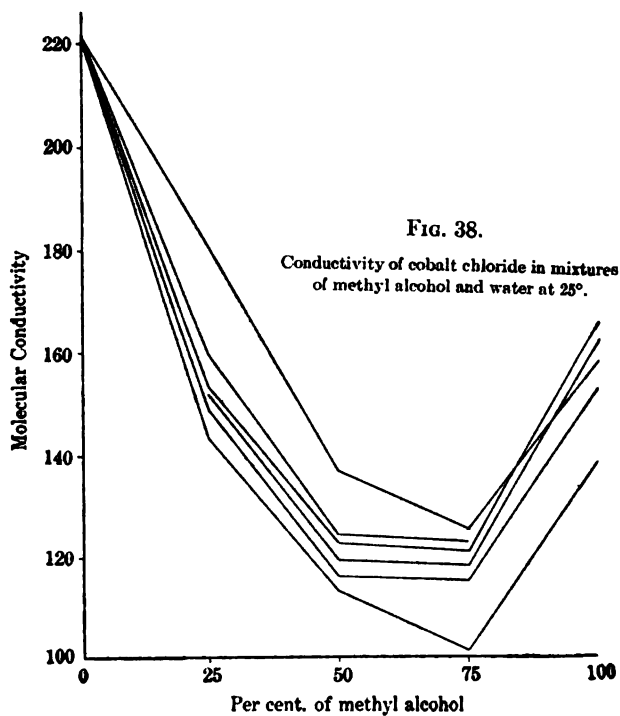
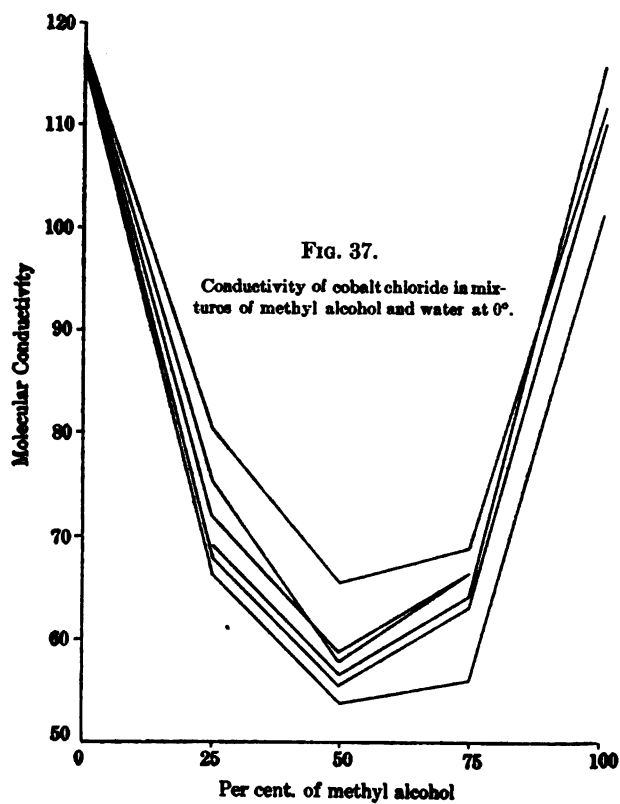
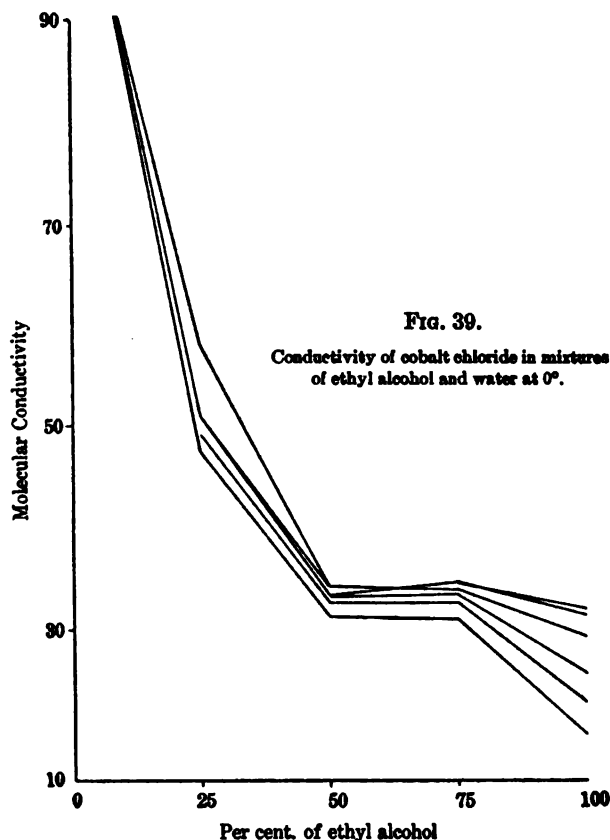


Fig. 43 for dissociation corresponds to fig. 39 for molecular conductivity. The relation between these two figures is similar to the relation between figs. 43 and 40. In both cases the mixed solvents are ethyl alcohol and water. In this case we have a binary salt, and the curves for figs. 41 and 43 are strikingly similar.



The curves representing dissociation in ethyl alcohol-water mixtures are sometimes upward curves, taking a direction opposite to that of the curves representing conductivity, which are downward curves. This fact is especially apparent when fig. 35, giving the curves for the conductivity of potassium iodide in mixtures of ethyl alcohol and water at 0°, is compared with fig. 41, which gives the curves for the dissociation of these same solutions. This plainly indicates that the greatly diminished conductivity in mixed solvents is due not to diminished dissociation, but to the other factor conditioning conductivity, viz, diminished velocity of the ions through the solution. Though it had been previously pointed out that this diminished conductivity is due almost entirely to increased viscosity of the mixed solvent, it was not definitely known what the magnitude of the dissociation in these mixed solvents is, nor was it suspected that this dissociation might be greater in the mixed than in the pure solvents, as is shown to be the case by the curves for dissociation, some of these curves having maxima, while those of conductivity have decided minima. These facts are quite marked where ethyl alcohol-water mixtures are used as solvent. In such cases

the increased viscosity, on the one hand, diminishes the conductivity, and the decreased dissociation, on the other, increases the conductivity. The viscosity in this case, since it is the more potent factor, causes the large minima in the curves for conductivity. These minima would be more marked than they are were it not for the slightly increased dissociation.

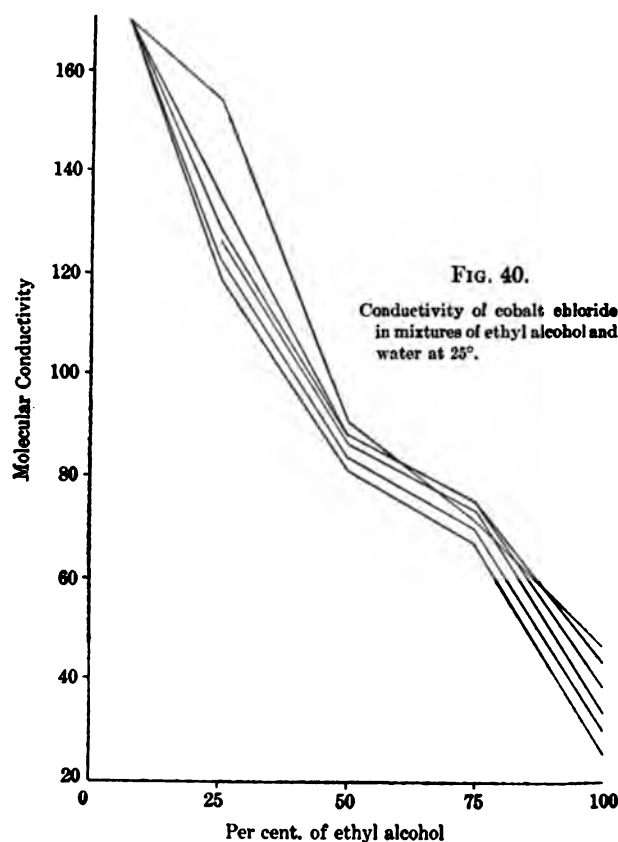


Table 70 gives the  $\mu_{\infty}$  values of molecular conductivity for the various salts studied both in methyl and in ethyl alcohols at 0° and at 25°, whenever such values could be found. The values without the brackets were determined experimentally. Those within the brackets could not be determined experimentally because of the great dilutions and consequently unavoidable errors, but were calculated by a method given below.

#### BINARY ELECTROLYTES AND TERNARY ELECTROLYTES.

An examination of the table reveals the fact that there is some relation between the maxima for each salt in the different solvents at any given temperature. It was suspected that this relation is a constant and that the following equation would hold:

$$\frac{\mu_{\infty} \text{ methyl}}{\mu_{\infty} \text{ ethyl}} = \text{constant.}$$

This equation was then applied with the following results:

<i>Binary Electrolytes:</i>		<i>c</i>		<i>c</i>	
LiNO <sub>3</sub>	at 0°	=2.37	NH <sub>4</sub> Br	at 25°	=2.44
NaI	0°	=2.37	NaI	25°	=2.17

*Ternary Electrolytes:*

$\text{CoCl}_2$  at  $0^\circ$   $=3.68$ .

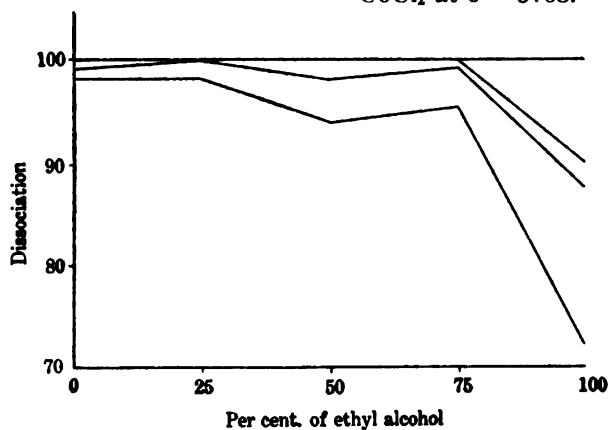


FIG. 41.

Dissociation of potassium iodide in mixtures of ethyl alcohol and water at  $0^\circ$ .

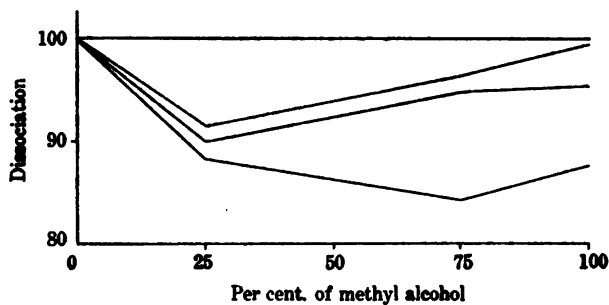


FIG. 42.

Dissociation of cobalt chloride in mixtures of methyl alcohol and water at  $0^\circ$ .

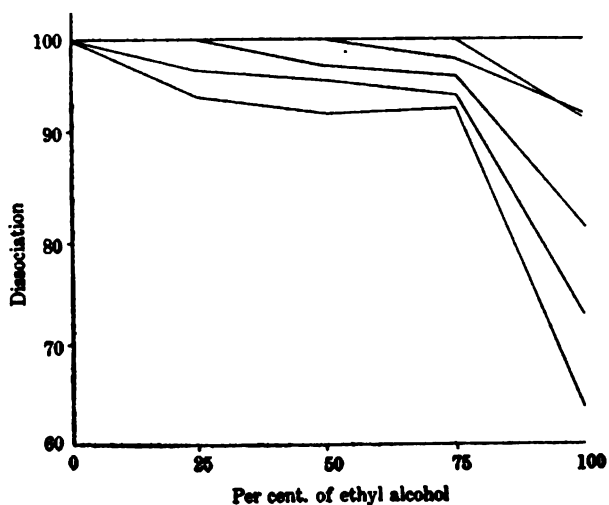


FIG. 43.

Dissociation of cobalt chloride in mixtures of ethyl alcohol and water at  $0^\circ$ .

These facts make it appear probable that there is approximately such a constant for binary electrolytes and another for ternary electrolytes. These data are not sufficient, however, to give a final value to such constants. Further investigations will be required for this purpose. Most of these maxima occur at dilutions of  $V = 12,800$  to  $V = 51,200$ . At these dilutions it is very difficult to obtain accurate results, and the values for the constant are probably within the limits of experimental error.

The value for the constant between methyl and ethyl alcohols for binary electrolytes appears to be very nearly 2.37. We have obtained but one value for ternary electrolytes, which is 3.68. That is nearly  $1.5 \times 2.37$ . The latter value (3.56) is probably the more nearly correct. The factor 1.5 is employed, since this expresses the ratio of ions present between binary and ternary electrolytes at complete dissociation.

With the data in hand we proceeded to test further the accuracy of the above equation, by supplying by calculation in table 70 those  $\mu_{\infty}$  values which could not be determined experimentally. The value of the constant was taken as 2.37 for binary electrolytes, and 3.56 for ternary electrolytes. The calculated value for potassium iodide in methyl alcohol at  $0^{\circ}$  from the value in ethyl alcohol would be 77.5. An examination of table 64 reveals the fact that this value is probably very nearly correct. For  $25^{\circ}$  it would be 112.6. Again, from the same table this is probably correct. Ammonium bromide in ethyl alcohol at  $0^{\circ}$  would be equal to 30.3. This, too, as indicated by table 64, is probably nearly correct. Potassium sulphocyanate in methyl alcohol at  $25^{\circ}$  would have a value of 110.4. Table 64 indicates that this value is probably correct to within the limits of experimental error. Lithium nitrate gives a value of 96.7 in methyl alcohol at  $25^{\circ}$ ; compared with table 64 this would seem to be nearly correct.

With ternary electrolytes there are only three cases to which this equation can be applied. Copper chloride in ethyl alcohol at  $0^{\circ}$  would give a value of 24.8, and cobalt chloride in ethyl alcohol at  $25^{\circ}$  would give 46.7 as the value for the maximum in conductivity. In table 64, at  $0^{\circ}$ , a maximum is reached at  $V = 25,600$ . The maxima at the different temperatures as a rule do not occur very far apart. We believe that the value 46.7 is very nearly correct for the maximum for cobalt chloride in ethyl alcohol at  $25^{\circ}$ . The only two values which do not fit into the table are those for potassium cyanide in methyl alcohol at  $0^{\circ}$ , and for copper chloride in ethyl alcohol at  $25^{\circ}$ . The latter, however, is not far from what we might expect it to be.

We believe from the above results that the ratio between the maxima in molecular conductivity for different salts in methyl alcohol, and the maxima for the same salts in ethyl alcohol is probably constant for all binary electrolytes; that for all ternary electrolytes it is a constant of different value, and that there is a definite relation between these two constants.

Jones, in an article on "The Electrolytic Dissociation of Certain Salts in Methyl and Ethyl Alcohols, as Measured by the Boiling-Point Method," gives table 72, which expresses "the dissociation values of the above alcohols as calculated from data obtained by the boiling-point method." The ratios of these values were calculated and are also expressed in the table.

Leaving out the value 1.8 for sodium iodide, which is evidently erroneous, we find as a mean from the other values of the binary electrolytes 2.37, which, it will be

remembered, is the same as the value obtained above by the conductivity method for the ratio between the maxima in the different alcohols. The figure in this table for the one ternary electrolyte is not so great as that determined by the conductivity method, and yet it is possible that more data would give comparable values.

TABLE 72.—*Dissociation in Methyl and Ethyl Alcohols.*

Substance.	Dilution normal.	Dissociation in methyl alcohol.	Dissociation in ethyl alcohol.	Ratio.
		<i>p. ct.</i>	<i>p. ct.</i>	
KI.....	0.1	52	25	2.08
NaI.....	0.1	60	33	1.8
NaBr.....	0.1	60	24	2.5
NH <sub>4</sub> Br.....	0.2	49	21	2.3
CH <sub>3</sub> COOK.....	0.1	36	16	2.3
CH <sub>3</sub> COONa.....	0.1	38	14	2.7
Ca(NO <sub>3</sub> ) <sub>2</sub> .....	0.1	15	5	3.0

The boiling-point data in this work were obtained by means of the boiling-point apparatus used by Jones.<sup>1</sup> Both solvents were carefully purified and dried.

Table 73 gives the dissociation of certain salts as calculated by both the conductivity and boiling-point methods.

It will readily be seen from table 73 that the dissociation values as determined by conductivity are higher than those found by the boiling-point method in both methyl and ethyl alcohols. This may possibly be due to a polymerization of the undissociated molecules in the solvent in question. This would give too low dissociation as measured by the boiling-point method, since this method takes into account both the molecules and the ions, while the conductivity method deals only with the ions.

TABLE 73.—*Dissociation of Salts as Determined by the Conductivity and Boiling-point Methods.*

Salt.	Solvent.	Dissociation from conductivity method.	Dissociation from boiling-point method.
		<i>p. ct.</i>	<i>p. ct.</i>
KI.....	Methyl.	65	49
KI.....	Ethyl.	49	26
NaI.....	Methyl.	75	61
NH <sub>4</sub> Br.....	Methyl.	71	47
NH <sub>4</sub> Br.....	Ethyl.	40	20

## SUMMARY.

We have measured the conductivity of various salts in pure methyl and ethyl alcohols at very high dilutions, and also in mixtures of methyl and ethyl alcohols with water. In many of these measurements we have found the value of  $\mu_{\infty}$ .

Many of these values were found to occur at concentrations between  $V=3,200$  and  $V=51,200$ .

A constant ratio was found between the values of  $\mu_{\infty}$  for several binary electrolytes in methyl alcohol and in ethyl alcohol, and the ratio for one ternary electrolyte

<sup>1</sup>Zeit. phys. Chem., 31, 114 (1899) (Jubelband zu van't Hoff).

was worked out. These facts indicate that there is a definite relation between these two ratios.

We have found minima in most of the curves for mixed solvents.

We have tabulated the dissociation of several salts in methyl alcohol and ethyl alcohol as determined by the boiling-point method.

The following work is a continuation of that already discussed.<sup>1</sup> In our earlier work we measured the conductivity of certain salts in very dilute solutions of ethyl alcohol and methyl alcohol. The salts employed were potassium iodide, ammonium bromide, potassium sulphocyanate, lithium nitrate, sodium iodide, calcium nitrate, cobalt chloride, and copper chloride. The conductivities of these salts were measured in solutions ranging in concentration from N/1600 to N/51200. The conductivities of these salts in more concentrated solutions had been previously determined by Jones and his coworkers.

In our former work a well-defined maximum in conductivity with increasing dilution was noted in solutions of a number of salts. Certain relations between these maxima were pointed out. The ratio between  $\mu_{\infty}$  for a certain salt in methyl alcohol and  $\mu_{\infty}$  for the same salt in ethyl alcohol was found to be a constant for different binary salts. The following values were obtained for  $c = \mu_{\infty}$  methyl alcohol/ $\mu_{\infty}$  ethyl alcohol.

<i>Binary Electrolytes:</i>		<i>c</i>
LiNO <sub>3</sub>	at 0°	=2.37
NaI	at 0°	=2.37
NH <sub>4</sub> Br	at 25°	=2.44
NaI	at 25°	=2.17

<i>Ternary Electrolytes:</i>		<i>c</i>
CoCl <sub>2</sub>	at 0°	=3.68

The conductivities of other salts at the same high dilutions have now been measured, with the object of seeing whether the relations given above are general. The salts used were sodium bromide, lithium bromide, and cobalt bromide. The work with potassium sulphocyanate in methyl alcohol was repeated, and more satisfactory results obtained.

Most of the measurements were made at the dilution of complete dissociation. The values of  $\mu_{\infty}$  for the same salt in methyl and ethyl alcohols are then compared with each other, and also with the value of  $\mu_{\infty}$  for the same salt in water. The apparatus employed is the same as that previously described, with some minor improvements. The same cells, with concentric platinum cylinders as electrodes, were used. One cell having the electrodes closer together and a smaller constant was also employed.

Both salts and solvents were purified with special care. A solution of a certain concentration was then prepared as the mother-solution, and from it the other solutions were made. Some of the solutions were as dilute as N/102400.

The precautions observed were the same as those previously discussed. In addition, greater care was exercised in purifying the methyl alcohol. It is very difficult to get methyl alcohol in large quantities in such a state of purity that its specific conductivity is low enough to obtain good results for such dilute solutions. It was

<sup>1</sup>Amer. Chem. Jour., 43, 232 (1911).



found that the conductivity of methyl alcohol could be much reduced by treating the alcohol with a little dilute sulphuric acid. The best results were obtained when the alcohol was in contact with the acid not more than twelve hours. The alcohol was then distilled from the acid and boiled with, and distilled from lime at least twice. The results obtained are given in tables 74 and 75.

TABLE 74.—*Conductivities of Sodium Bromide, Lithium Bromide, Potassium Sulphocyanate, and Cobalt Bromide in Methyl Alcohol and Ethyl Alcohol at 0° and 25°.*

V	Sodium bromide in methyl alcohol.		Sodium bromide in ethyl alcohol.		Lithium bromide in methyl alcohol.		Lithium bromide in ethyl alcohol.		Potassium sulphocyanate in methyl alcohol.		Cobalt bromide in methyl alcohol.		Cobalt bromide in ethyl alcohol.	
	$\mu_0$	$\mu_{25^\circ}$	$\mu_0$	$\mu_{25^\circ}$	$\mu_0$	$\mu_{25^\circ}$	$\mu_0$	$\mu_{25^\circ}$	$\mu_0$	$\mu_{25^\circ}$	$\mu_0$	$\mu_{25^\circ}$	$\mu_0$	$\mu_{25^\circ}$
800	53.0	77.4	19.9	33.6	40.9	57.2	.....	.....	.....	.....	19.0	23.6	57.9	77.3
1,600	58.2	83.9	23.1	36.5	44.5	64.8	17.2	27.8	70.7	99.9	21.6	27.5	61.3	82.0
3,200	62.3	88.6	24.0	38.3	45.6	68.7	18.3	28.9	75.8	106.2	24.9	32.4	62.2	87.4
6,400	63.8	91.3	24.6	39.6	48.2	69.8	18.3	29.3	72.9	102.9	29.1	37.0	64.7	95.1
12,800	64.1	92.8	24.9	40.2	47.8	73.7	18.4	28.9	73.9	104.5	33.1	44.2	66.9	106.7
25,600	64.6	93.3	24.6	40.2	49.5	74.6	18.3	29.4	72.1	105.4	36.8	50.6	70.1	106.6
51,200	69.1	101.0	21.0	37.6	.....	.....	18.3	30.1	86.1	132.2	38.6	65.9	96.2	124.0
102,400	.....	.....	.....	32.9	.....	.....	18.1	27.8	.....	.....	.....	.....	.....	.....

TABLE 75.—*Ratios of Conductivities and Fluidities.<sup>1</sup>*

Flu. W Flu. E	Temp.	$\frac{\mu_\infty W}{\mu_\infty E}$	Flu. M Flu. W	Temp.	$\frac{\mu_\infty M}{\mu_\infty W}$	Flu. M Flu. E	Temp.	$\frac{\mu_\infty M}{\mu_\infty E}$
.....	0°	LiNO <sub>3</sub> 2.26 NaI 2.31 KI 2.33 NaBr 2.44	.....	0°	KI 1.01 NaI 1.02 LiNO <sub>3</sub> 1.05 NaBr 1.05	.....	0°	NaBr 2.32 LiNO <sub>3</sub> 2.37 NaI 2.37 KCNS 2.53 LiBr 2.60
0.995	.....	.....	2.18	.....	.....	.....	.....	.....
.....	25°	CoCl <sub>2</sub> 2.33 CoCl <sub>2</sub> 3.70	.....	25°	.....	2.17	25°	.....
.....	.....	.....	.....	.....	CoCl <sub>2</sub> 1.03 CoCl <sub>2</sub> 0.99	.....	.....	CoCl <sub>2</sub> 2.44 CoCl <sub>2</sub> 3.67
.....	.....	.....	.....	.....	.....	.....	.....	NaI 2.17 KCNS 2.27 LiBr 2.38 NH <sub>4</sub> Br 2.44 NaBr 2.59
0.817	.....	.....	1.65	.....	.....	2.27	.....	.....
.....	.....	.....	.....	.....	.....	.....	.....	2.37

<sup>1</sup>W=water; M=methyl alcohol; E=ethyl alcohol.

Table 74 gives the conductivities of sodium bromide in methyl alcohol at both 0° and 25°. At 0° we have complete dissociation probably at 6,400 liters. At 25° complete dissociation is not attained until a dilution of 12,800 liters is reached.

Table 74 gives the conductivities of sodium bromide in ethyl alcohol at 0° and 25°. Complete dissociation is reached at both temperatures at a dilution of 12,800 liters. At the volume 102,400 there is a marked decrease in conductivity, probably due to the great solvation at this extremely high dilution. The same fact may be noticed in several other tables where ethyl alcohol is used as a solvent.

Table 74 gives the conductivity of lithium bromide in methyl alcohol. At 0° complete dissociation probably is reached at 6,400 liters. At 25° there is no maximum in conductivity, but the rate of increase is much smaller above 3,200 liters than it is at greater concentrations, indicating that the maximum is nearly reached.

Table 74 gives the conductivity of lithium bromide in ethyl alcohol. At 0° there is complete dissociation at 3,200 liters. At 25° it is complete at 6,400 liters. For both temperatures at higher dilutions the conductivity remains almost constant up to a dilution of 102,400 liters, where, at 25°, there is a marked decrease in the conductivity.

Table 74 gives the conductivity of potassium sulphocyanate in methyl alcohol. This is a repetition of work previously done. We have now obtained more concordant results. Here, complete dissociation is reached at both temperatures at 3,200 liters.

Table 74 gives the conductivity of cobalt bromide in both methyl alcohol and ethyl alcohol. Here, there is no maximum in conductivity. This is probably due to the fact that cobalt bromide is much solvated.

Table 75 gives the ratios of the values of  $\mu_{\infty}$  for a number of salts in the following solvents: Water and ethyl alcohol, methyl alcohol and water, and methyl alcohol and ethyl alcohol. When we consider the large magnitude of the experimental error in working at these great dilutions, it is quite probable that the relation  $\mu_{\infty}$  for one solvent/ $\mu_{\infty}$  for another solvent =  $c$ , holds where the salts have approximately the same degree of solvation.

That there is a constant relation between the values of  $\mu_{\infty}$  for different salts in different solvents we would expect. When a certain salt in two different solvents is completely dissociated, we have either the same number of ions present or, relative to the concentration, the same number of ions present.

When the point of complete dissociation is reached at the same dilution in both solvents, we have the same number of ions present in the same volume of the two solvents. When such a point of complete dissociation exists at different dilutions in solutions of the two solvents, the number of ions in equal volumes of the two solutions varies directly as the concentration, and we have, relative to the concentration, the same number of ions present.

Conductivity is a function of the number of ions present and the velocity with which these ions move. Since, at the complete dissociation of a salt in solutions of two different solvents the number of ions is actually the same, or relative to the concentration the same, we can eliminate this factor—the number of ions—and consider only the velocities with which these ions move.

Two factors primarily determine ionic velocity, the ionic mass and volume, and the fluidity of the solution, which is, of course, the reciprocal of the viscosity. Assuming that the ionic masses and volumes of a certain salt in two different solvents at complete dissociation remain the same, then the velocities of the ions ought to vary as the fluidities of the respective solvents. Since the number of ions in the two solvents at the same dilution of the solutions is the same, the ionic masses and volumes being the same, the conductivities ought to vary directly as the fluidities of the solvents; the ratio between the values of  $\mu_{\infty}$  in the various solvents ought to

be the same as the ratio of the fluidities of these solvents. This, however, is not the case. If the ratios between the values of  $\mu_{\infty}$  for the salts in the two solvents are not the same as the ratios between the values for the fluidities of these solvents, the mass and probably the volumes of the solvated ions must differ in the two different solutions.

The fluidity of methyl alcohol at 0° is 123.9, while that of ethyl alcohol is 56.24. Since the fluidity of methyl alcohol is much greater than that of ethyl alcohol, we would expect the ions of a dissolved salt to move much faster in methyl alcohol, and, consequently, the conductivity of a solution of a salt at any concentration would be much greater in methyl than in ethyl alcohol. At complete dissociation, where the number of ions is the same in both solvents, we would expect the conductivity in methyl alcohol to be as much greater than that in ethyl alcohol as the fluidity of the former is greater than that of the latter. We would expect a direct relation between fluidity and conductivity.

Jones and his coworkers have shown that there is solvation in solutions in water, methyl alcohol, ethyl alcohol, and solvents in general; and that this solvation increases with dilution. From this we know that at complete dissociation solvation is greater than at any dilution short of complete dissociation.

Since a molecule of methyl alcohol is much heavier than one of water, the ion, for equal solvation, would be loaded down more in the former solvent, and the conductivity in methyl alcohol would be less than in water, even if the fluidities were the same. Again, the molecule of ethyl alcohol is heavier than the molecule of methyl alcohol. The equally solvated ion would, therefore, be heavier in ethyl alcohol and the conductivity less.

Table 75<sup>1</sup> gives the ratios of the fluidities of three solvents—water, methyl alcohol, and ethyl alcohol; also the ratio of  $\mu_{\infty}$  for certain salts in these solvents at both 0° and 25°. Water and ethyl alcohol are first compared. Their fluidities are nearly the same, hence their ratio is nearly unity. The ratios between the values of  $\mu_{\infty}$  for four salts in these two solvents are given. The mean of these values is 2.33 with a minimum of 2.26 and a maximum of 2.44. This mean ratio of the values is much greater than the ratio of the fluidity values of the two solvents, indicating that the ion in ethyl alcohol moves much more slowly, compared with its velocity in water, than we would expect from a comparison of the fluidities of the solvents. The only explanation of this fact seems to be that the ion is loaded down much more in ethyl alcohol than in water, and, hence, its velocity diminished, giving a much lower conductivity. The only way in which it could be loaded down is by one or more molecules of the solvent being united with the ion.

In the second column of table 75 water and methyl alcohol are compared. The fluidity of methyl alcohol is much greater than that of water. It is 2.18 times as great at 0°. There are four  $\mu_{\infty}$  ratios. The mean is 1.03. The maximum is 1.05 and the minimum is 1.01. The fact that the fluidity of methyl alcohol is much greater than that of water, while the conductivity of salts in methyl alcohol is but little greater, indicates that in methyl alcohol the ion is loaded down more than in

<sup>1</sup>The values for  $\mu_{\infty}$  of the various salts in water as a solvent given in table 75 are taken from the work of Jones and Getman (Zeit. phys. Chem., 49, 385 (1904)).

water, and its velocity more retarded. This, of course, we would expect from the masses of the molecules alone, since those of methyl alcohol are so much greater than those of water.

In the third column, methyl alcohol and ethyl alcohol are compared. The fluidity of methyl alcohol is 2.17 times as great as that of ethyl alcohol at 0°; while the mean of the conductivity ratios is 2.44. This would indicate that in ethyl alcohol the ions are loaded down more than in methyl alcohol, which, again, we would expect. This is the case at both 0° and 25°. The difference is, however, much less at 25° than at 0°. At 25° the ratios of fluidity and conductivities are more nearly equal. This would indicate that at the higher temperatures the ions are less retarded and, accordingly, less solvated, as Jones and Bassett<sup>1</sup> have pointed out.

The fact that the equation

$$\mu_{\infty}s/\mu_{\infty}s' = c$$

where  $s$  and  $s'$  are any two of the solvents above mentioned, holds for the values in table 75 is in itself important. But it further shows approximately which salts are solvated to the same extent in any given solvent, since it holds only in such cases. For such salts as are not solvated to the same extent in a given solvent the equation will, of course, not hold.

We have worked with one salt, cobalt chloride, which is very hygroscopic, and which has been shown by Jones and his coworkers to be strongly hydrated in aqueous solutions. This salt shows a greater departure in the ratios of its conductivities from the ratios of fluidities than is shown by the other salts that we studied. From the results in the column  $\mu_{\infty}W/\mu_{\infty}E$  we see that cobalt chloride is much more loaded down in ethyl alcohol than it is in water. The value of the ratio of  $\mu_{\infty}$  in the two solvents, 3.70, is greater than that of the other salts, 2.33, and much greater than the value of the fluidity ratio of the two solvents, which is 0.995.

From the column  $\mu_{\infty}M/\mu_{\infty}W$  we see that the ions of cobalt chloride are loaded down more in methyl alcohol than in water, and that the ratios of the conductivities deviate more from the ratios of fluidities than in the case of the other salts; but this deviation ought not to be as great as in the case of water and ethyl alcohol, since there is not so much difference between the masses of the molecules of methyl alcohol and water as there is between those of ethyl alcohol and water. Comparing the figures in this column we find that this is the case, since 0.99, the value of the ratio of the conductivities of cobalt chloride, is less than 1.03, the ratio for the other salts, and very much less than 2.18, the ratio of the fluidities of the two solvents.

We would expect the cobalt chloride ions to be loaded down to the greatest extent in ethyl alcohol, and that the conductivity in ethyl alcohol would be lower than in methyl alcohol. This difference should be greater than that of the other salts which are less solvated. We would expect the ratio  $\mu_{\infty}M/\mu_{\infty}E$  for this salt to show a greater departure from the ratio of the fluidities of the two solvents than is shown by the other salts. A comparison of the figures in column  $\mu_{\infty}M/\mu_{\infty}E$  shows this to be the case.

<sup>1</sup>Amer. Chem. Journ., 34, 280 (1905).



## WORK OF E. G. MAHIN.

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It has been shown that water hydrates salts in more concentrated solutions, and that this hydration increases with the dilution, as we would expect from the mass action of the solvent. If in water these salts are solvated, it is evident from the above facts that in methyl alcohol there is a larger mass of the solvent in combination with the ion. This does not necessarily indicate that in the latter case there are more molecules of the solvent in combination with the ion. There may be the same number, or even less, in combination, but the molecules of methyl alcohol being so much heavier might cause the difference in conductivity. In ethyl alcohol also there is a larger molecular mass than in water or in methyl alcohol, but here, again, the difference between the ratios may be due to the heavier molecules of ethyl alcohol.

It is evident that this factor of solvation at complete dissociation plays a rôle in our present method for calculating dissociation by means of the conductivity of the solution. Here we employ the equation  $\alpha = \mu_s / \mu_\infty$ . In the above discussion  $\mu_\infty$  is shown not to be a true function of the actual number of ions present, but is smaller than it ought to be in consideration alone of the number of ions present. Furthermore, it has been shown that there is solvation in more concentrated solutions also; hence,  $\mu_s$  is not a function only of the number of ions present in the solution in question. The deviations of the values of  $\mu_s$  and  $\mu_\infty$  from the true values are probably of the same order of magnitude, if not very nearly equal, so that the validity of the equation in calculating conductivity is probably not seriously affected.

### FACTS ESTABLISHED..

We have measured the conductivities of very dilute solutions of a number of salts in methyl alcohol and ethyl alcohol.

In most cases the values of  $\mu_\infty$  were found. These values bear a definite relation to one another.

It was found that the ratio of the value of  $\mu_\infty$  for a certain salt in one solvent and the value of  $\mu_\infty$  for the same salt in another solvent, is nearly constant for salts which are solvated to approximately the same extent.

In cases where one salt is solvated very much more than another, the value of  $\mu_\infty$  is generally less for the more solvated salt.

We have compared the ratios of  $\mu_\infty$  for certain salts in two different solvents, with the ratios of the fluidities of these solvents. In all cases the former ratios show a departure from the latter, the value of  $\mu_\infty$  in the solvent which has the greater molecular mass always being less than we would expect from the ratio of the fluidities alone of the two solvents. Those salts which are known to be solvated to the greatest extent show the greatest difference between these ratios.

A large amount of work has been done with the object of learning something about the electrochemistry of organic solvents and of binary mixtures of these liquids. This is especially true with regard to the relations existing between conductivity and viscosity of solutions in such solvents. A full account of the work that has been done in this laboratory has been published as a monograph by Jones<sup>1</sup> and coworkers, and the electrochemistry of nonaqueous solvents has been extensively discussed by Carrara.<sup>2</sup>

In the following pages are recorded the results of a few preliminary experiments, which were made with the object of determining whether any essentially new principles were to be discovered by increasing the number of components of a solvent mixture from two to three. It would be, of course, impossible to predict whether or not the mutual action of three solvents upon each other would be the average action of the three possible pairs of components. No extensive study of this matter has, as yet, been made. We have measured the viscosity of ternary mixtures of water, methyl alcohol, ethyl alcohol, and acetone, and the conductivity of lithium nitrate in these mixtures. (Tables 76 to 82.) The materials, apparatus, and method of making the measurements were essentially the same as outlined in earlier articles. The following example will serve to indicate the method of designating the solvent mixtures: "Acetone (75 per cent methyl alcohol and water)" indicates a mixture of solvents made by adding stated amounts (per cent by volume) of acetone to a mixture of methyl alcohol and water which contains 75 per cent, by volume, of methyl alcohol.

TABLE 76.—*Conductivity of Lithium Nitrate in Acetone (85, 50, and 75 per cent Methyl Alcohol and Water).*

V	Acetone (25 per cent methyl alcohol and water).									
	At 0°, per cent acetone.					At 25°, per cent acetone.				
	0 p.ct.	25 p.ct.	50 p.ct.	75 p.ct.	100 p.ct.	0 p.ct.	25 p.ct.	50 p.ct.	75 p.ct.	100 p.ct.
10	27.26	23.08	23.13	25.80	9.67	56.46	48.07	44.78	40.31	10.87
50	29.41	24.50	26.60	33.10	14.07	61.51	51.65	51.89	55.29	15.64
100	30.11	26.07	27.37	35.50	18.1	63.53	55.43	53.88	59.78	19.5
200	31.06	.....	.....	38.22	23.8	65.72	.....	.....	64.80	25.3
400	31.35	30.18	28.91	40.54	30.6	66.41	64.05	57.42	68.85	32.4
800	31.62	31.85	29.27	42.03	43.4	66.94	66.63	58.21	71.78	45.5
1,600	32.16	.....	29.73	43.21	55.3	68.20	.....	58.40	73.16	59.8
Acetone (50 per cent methyl alcohol and water).										
10	21.86	22.54	25.15	28.09	9.67	44.58	43.79	44.42	42.77	10.87
50	23.91	25.55	29.57	37.62	14.07	49.41	50.18	53.11	58.37	15.64
100	24.79	26.57	31.08	41.25	18.1	51.44	52.32	55.90	64.40	19.5
200	25.37	27.11	32.55	44.28	23.8	52.79	53.67	59.02	69.82	25.3
400	25.47	28.70	34.14	47.31	30.6	53.10	55.05	62.03	74.56	32.4
800	26.10	28.62	34.17	48.52	43.4	54.32	56.50	64.35	77.97	45.5
1,600	26.94	30.26	35.35	50.40	55.3	56.50	57.95	64.41	80.10	59.8
Acetone (75 per cent methyl alcohol and water).										
10	24.16	26.32	29.56	31.55	9.67	43.06	44.63	46.21	43.16	10.87
50	27.56	30.99	36.94	44.86	14.07	49.58	53.29	58.56	63.32	15.64
100	28.67	32.99	38.90	50.16	18.1	51.96	56.06	62.36	71.28	19.5
200	29.60	34.11	41.90	55.20	23.8	53.80	59.20	67.37	79.26	25.3
400	29.82	34.75	42.96	58.80	30.6	54.63	60.23	69.32	84.82	32.4
800	30.62	35.30	44.31	61.75	43.4	55.72	61.24	71.51	89.78	45.5
1,600	31.45	36.71	45.45	64.84	55.3	58.06	63.88	73.49	94.22	59.8

<sup>1</sup>Carnegie Institution of Washington Pub. No. 80 (1907).

<sup>2</sup>Ahren's Sammling, 12, No. 11 (1906).

TABLE 77.—*Temperature Coefficients of Conductivity of Lithium Nitrate in Mixtures of Acetone, Methyl Alcohol, and Water.*

	At 0°, per cent acetone.					
	V	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
In acetone (25 per cent methyl alcohol and water).....	10	0.0428	0.0433	0.0374	0.0225	0.0049
	50	0.0437	0.0443	0.0380	0.0268	0.0045
	100	0.0444	0.0450	0.0387	0.0273	0.0031
	200	0.0446	.....	.....	0.0278	0.0025
	400	0.0447	0.0449	0.0394	0.0279	0.0023
	800	0.0447	0.0437	0.0395	0.0283	0.0019
	1,600	0.0448	.....	0.0386	0.0277	0.0032
In acetone (50 per cent methyl alcohol and water).....	10	0.0416	0.0377	0.0314	0.0209	0.0049
	50	0.0427	0.0385	0.0318	0.0221	0.0045
	100	0.0430	0.0388	0.0319	0.0224	0.0031
	200	0.0432	0.0391	0.0325	0.0231	0.0026
	400	0.0434	0.0367	0.0327	0.0230	0.0023
	800	0.0433	0.0390	0.0326	0.0243	0.0019
	1,600	0.0439	0.0366	0.0326	0.0236	0.0032
In acetone (75 per cent methyl alcohol and water).....	10	0.0313	0.0278	0.0225	0.0151	0.0049
	50	0.0320	0.0288	0.0234	0.0165	0.0045
	100	0.0325	0.0290	0.0241	0.0168	0.0031
	200	0.0327	0.0294	0.0243	0.0174	0.0025
	400	0.0333	0.0292	0.0245	0.0177	0.0023
	800	0.0328	0.0294	0.0246	0.0182	0.0019
	1,600	0.0338	0.0296	0.0247	0.0181	0.0032

TABLE 78.—*Conductivity of Lithium Nitrate in Acetone (25, 50, and 75 per cent Ethyl Alcohol and Water).*

V	Acetone (25 per cent ethyl alcohol and water).									
	At 0°, per cent acetone.					At 25°, per cent acetone.				
	0 p.ct.	25 p.ct.	50 p.ct.	75 p.ct.	100 p.ct.	0 p.ct.	25 p.ct.	50 p.ct.	75 p.ct.	100 p.ct.
10	19.66	18.74	20.71	23.93	9.67	46.70	42.51	41.31	39.75	10.87
50	21.03	20.44	23.64	30.73	14.07	51.11	47.25	47.93	52.10	15.64
100	21.51	21.05	24.61	33.31	18.1	52.37	48.76	50.12	56.84	19.5
200	22.03	21.70	25.46	35.20	23.8	54.00	50.42	52.19	60.51	25.3
400	22.20	22.15	25.78	36.74	30.6	54.60	51.76	52.93	63.21	32.4
800	22.48	22.04	26.38	37.96	43.4	55.39	51.62	54.17	65.59	45.5
1,600	24.54	22.83	26.69	40.74	55.3	58.59	52.96	54.78	70.11	59.8
Acetone (50 per cent ethyl alcohol and water).										
10	12.53	15.98	19.85	23.80	9.67	31.82	34.54	36.95	36.77	10.87
50	13.57	17.89	23.62	32.49	14.07	35.34	39.43	44.64	51.27	15.64
100	14.02	18.63	25.13	35.90	18.1	36.56	41.23	47.69	58.06	19.5
200	14.42	19.21	26.13	38.84	23.8	37.88	42.64	49.88	62.36	25.3
400	14.60	.....	26.98	39.67	30.6	38.31	.....	51.71	63.83	32.4
800	14.88	19.33	.....	43.56	43.4	38.96	44.15	.....	68.75	45.5
1,600	14.88	20.56	30.23	46.13	55.3	39.35	45.56	53.86	71.67	59.8
Acetone (75 per cent ethyl alcohol and water).										
10	12.01	15.84	20.41	23.29	9.67	25.56	29.66	33.32	32.59	10.87
50	13.80	19.00	26.84	35.29	14.07	29.91	36.32	44.69	50.39	15.64
100	14.48	20.21	29.06	40.41	18.1	31.64	38.85	48.68	58.35	19.5
200	15.14	20.92	31.76	44.80	23.8	33.12	40.44	53.90	65.72	25.3
400	15.41	21.67	32.70	48.43	30.6	33.90	42.11	55.52	71.59	32.4
800	15.76	22.52	35.55	51.38	43.4	34.88	41.91	57.32	76.39	45.5
1,600	16.10	22.56	35.20	54.01	55.3	35.85	43.97	60.54	81.28	59.8



TABLE 79.—*Temperature Coefficients of Conductivity of Lithium Nitrate in Mixtures of Acetone, Ethyl Alcohol, and Water.*

	V	At 0°, per cent acetone.				
		0 p.ct.	25 p.ct.	50 p.ct.	75 p.ct.	100 p.ct.
In acetone (25 per cent ethyl alcohol and water).....	10	0.0550	0.0507	0.0398	0.0265	0.0049
	50	0.0572	0.0524	0.0411	0.0291	0.0045
	100	0.0574	0.0526	0.0414	0.0282	0.0031
	200	0.0581	0.0530	0.0420	0.0287	0.0025
	400	0.0584	0.0535	0.0421	0.0288	0.0023
	800	0.0585	0.0537	0.0422	0.0290	0.0019
	1,600	0.0555	0.0528	0.0421	0.0288	0.0032
In acetone (50 per cent ethyl alcohol and water).....	10	0.0614	0.0464	0.0341	0.0218	0.0049
	50	0.0642	0.0482	0.0356	0.0231	0.0045
	100	0.0643	0.0485	0.0359	0.0247	0.0031
	200	0.0650	0.0488	0.0364	0.0242	0.0025
	400	0.0649	.....	0.0367	0.0244	0.0023
	800	0.0647	0.0491	.....	0.0231	0.0019
	1,600	0.0658	0.0486	0.0313	0.0222	0.0032
In acetone (75 per cent ethyl alcohol and water).....	10	0.0451	0.0349	0.0253	0.0160	0.0049
	50	0.0467	0.0365	0.0267	0.0171	0.0045
	100	0.0474	0.0369	0.0270	0.0177	0.0031
	200	0.0475	0.0373	0.0378	0.0187	0.0025
	400	0.0480	0.0377	0.0278	0.0192	0.0023
	800	0.0485	0.0380	0.0283	0.0194	0.0019
	1,600	0.0491	0.0379	0.0288	0.0202	0.0032

TABLE 80.—*Conductivity of Lithium Nitrate in Methyl Alcohol (25, 50, and 75 per cent Ethyl Alcohol and Water).*

V	Methyl alcohol (25 per cent ethyl alcohol and water).									
	At 0°, per cent methyl alcohol.					At 25°, per cent methyl alcohol.				
	0 p.ct.	25 p.ct.	50 p.ct.	75 p.ct.	100 p.ct.	0 p.ct.	25 p.ct.	50 p.ct.	75 p.ct.	100 p.ct.
10	19.66	17.76	19.50	24.35	37.62	46.70	40.13	39.04	41.67	51.3
50	21.03	19.11	21.65	28.13	48.31	51.11	44.13	44.05	48.85	67.2
100	21.51	19.89	22.46	29.68	52.0	52.37	45.97	45.81	51.49	72.6
200	22.03	20.19	22.76	31.76	55.1	54.00	46.48	46.53	53.73	76.8
400	22.20	20.57	23.08	31.32	56.8	54.60	47.86	47.35	53.94	80.0
800	22.48	20.63	23.39	32.19	59.6	55.39	48.10	47.96	56.14	83.7
1,600	24.54	21.09	23.34	32.73	61.9	58.59	49.72	47.92	57.59	86.7
V	Methyl alcohol (50 per cent ethyl alcohol and water).									
	At 0°, per cent methyl alcohol.					At 25°, per cent methyl alcohol.				
	0 p.ct.	25 p.ct.	50 p.ct.	75 p.ct.	100 p.ct.	0 p.ct.	25 p.ct.	50 p.ct.	75 p.ct.	100 p.ct.
10	12.53	15.35	19.19	25.18	37.62	31.82	33.24	36.13	41.18	51.3
50	13.57	16.96	21.95	30.04	48.31	35.34	37.35	41.91	49.48	67.2
100	14.02	17.61	22.87	31.69	52.0	36.56	39.10	43.87	52.36	72.6
200	14.42	18.02	23.75	32.97	55.1	37.88	40.08	45.72	54.91	76.8
400	14.60	18.41	24.61	34.18	56.8	38.31	41.57	47.44	57.06	80.0
800	14.88	18.60	24.98	34.57	59.6	38.96	41.63	48.06	57.67	83.7
1,600	14.88	19.50	25.15	35.48	61.9	39.35	43.82	48.53	59.61	86.7

TABLE 80—Continued.

V	Methyl alcohol (75 per cent ethyl alcohol and water).									
	At 0°, per cent methyl alcohol.					At 25°, per cent methyl alcohol.				
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
10	12.01	15.46	20.00	26.46	37.62	25.56	29.28	34.09	40.91	51.3
50	13.80	17.96	23.82	32.38	48.31	29.91	34.77	41.20	50.50	67.2
100	14.48	19.03	25.22	34.69	52.0	31.64	36.93	43.89	54.35	72.6
200	15.14	19.72	26.11	36.17	55.1	33.12	38.41	45.52	56.89	76.8
400	15.41	20.32	26.77	37.46	56.8	33.90	39.81	46.82	59.08	80.0
800	15.76	20.55	27.15	38.51	59.6	34.88	40.52	47.51	60.86	83.7
1,600	16.10	20.82	27.54	39.55	61.9	35.85	41.34	48.39	62.84	86.7

TABLE 81.—Temperature Coefficients of Conductivity of Lithium Nitrate in Mixtures of Methyl Alcohol, Ethyl Alcohol, and Water.

V	In methyl alcohol (25 per cent ethyl alcohol and water).					In methyl alcohol (50 per cent ethyl alcohol and water).				
	Per cent, methyl alcohol.					Per cent, methyl alcohol.				
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
10	0.0550	0.0504	0.0400	0.0284	0.0145	0.0614	0.0466	0.0353	0.0254	0.0145
50	0.0572	0.0524	0.0414	0.0295	0.0157	0.0642	0.0481	0.0364	0.0258	0.0157
100	0.0574	0.0524	0.0415	0.0294	0.0155	0.0643	0.0488	0.0367	0.0262	0.0155
200	0.0581	0.0521	0.0417	0.0276	0.0147	0.0650	0.0492	0.0370	0.0266	0.0147
400	0.0584	0.0530	0.0420	0.0289	0.0172	0.0649	0.0503	0.0371	0.0267	0.0172
800	0.0585	0.0532	0.0420	0.0298	0.0162	0.0647	0.0495	0.0365	0.0267	0.0162
1,600	0.0555	0.0542	0.0422	0.0301	0.0160	0.0658	0.0499	0.0372	0.0272	0.0160

TABLE 82.—Viscosity and Fluidity of Mixtures of Acetone, Methyl Alcohol, and Water.

	Per cent acetone.	$\eta$ 0°	$\eta$ 25°	$\Phi$ 0°	$\Phi$ 25°	Temperature coefficients.
Acetone (25 per cent methyl alcohol and water).....	0	0.03286	0.01368	30.44	73.11	0.0561
	25	0.03386	0.01428	29.53	70.04	0.0549
	50	0.02597	0.01209	38.50	82.75	0.0460
	75	0.01310	0.00751	76.36	133.22	0.0303
	100	0.00429	0.00346	233.21	288.95	0.0096
Acetone (50 per cent methyl alcohol and water).....	0	0.03586	0.01541	27.81	64.89	0.0531
	25	0.02850	0.01340	35.09	74.65	0.0451
	50	0.01926	0.01514	51.92	99.96	0.0371
	75	0.00984	0.00620	101.63	161.40	0.0235
	100	0.00429	0.00346	233.21	288.95	0.0096
Acetone (75 per cent methyl alcohol and water).....	0	0.02461	0.01253	41.64	79.84	0.0463
	25	0.01824	0.00990	54.81	101.06	0.0338
	50	0.01203	0.00726	83.10	137.79	0.0263
	75	0.00705	0.00491	141.76	203.85	0.0175
	100	0.00429	0.00346	233.21	288.95	0.0096

From the results thus far obtained, it would seem that the viscosity and conductivity values in ternary mixtures are about what might be expected from the behavior of solutions in binary solvent mixtures. A series of experiments with a salt, such as potassium iodide, which shows no abnormality in any of the single solvents, would make possible a more exact comparison of experimental with calculated values.

TABLE 83.—Viscosity and Fluidity of Mixtures of Acetone, Ethyl Alcohol, and Water.

	Per cent acetone.	$\eta$ 0°	$\eta$ 25°	$\Phi$ 0°	$\Phi$ 25°	Temperature coefficients.
Acetone (25 per cent ethyl alcohol and water).....	0	0.05111	0.01745	19.57	57.30	0.0770
	25	0.04329	0.01644	23.10	60.83	0.0653
	50	0.02856	0.01288	35.02	67.63	0.0487
	75	0.01356	0.00770	73.74	129.88	0.0305
	100	0.00429	0.00346	233.21	288.95	0.0096
Acetone (50 per cent ethyl alcohol and water).....	0	0.06949	0.02298	14.39	43.51	0.0643
	25	0.04152	0.01693	24.09	79.05	0.0580
	50	0.02284	0.01123	43.78	89.05	0.0414
	75	0.01047	0.00648	95.54	154.41	0.0246
	100	0.00429	0.00346	233.21	288.95	0.0096
Acetone (75 per cent ethyl alcohol and water).....	0	0.04826	0.01983	20.72	50.41	0.0573
	25	0.02907	0.01341	35.63	74.56	0.0437
	50	0.01529	0.00853	65.41	117.21	0.0317
	75	0.00935	0.00637	106.93	156.87	0.0177
	100	0.00429	0.00346	233.21	288.95	0.0096

TABLE 84.—Viscosity and Fluidity of Mixtures of Methyl Alcohol, Ethyl Alcohol, and Water.

	Per cent acetone.	$\eta$ 0°	$\eta$ 25°	$\Phi$ 0°	$\Phi$ 25°	Temperature coefficients.
Methyl alcohol (25 per cent ethyl alcohol and water)....	0	0.05111	0.01745	19.57	57.30	0.0770
	25	0.04851	0.01862	20.61	53.70	0.0642
	50	0.03904	0.01702	26.29	58.76	0.0498
	75	0.02198	0.01160	45.49	86.24	0.0358
	100	0.00857	0.00583	116.71	171.60	0.0176
Methyl alcohol (50 per cent ethyl alcohol and water)...	0	0.06949	0.02298	14.39	43.51	0.0643
	25	0.04919	0.01994	20.33	50.14	0.0587
	50	0.03066	0.01481	32.41	67.62	0.0433
	75	0.01928	0.01083	51.88	92.34	0.0311
	100	0.00857	0.00583	116.71	171.60	0.0176
Methyl alcohol (75 per cent ethyl alcohol and water)...	0	0.04826	0.01983	20.72	50.41	0.0573
	25	0.03468	0.01614	28.83	61.97	0.0461
	50	0.02337	0.01216	42.86	82.23	0.0369
	75	0.01477	0.00880	67.70	113.62	0.0271
	100	0.00857	0.00583	116.71	171.60	0.0176

In 1902 Jones<sup>1</sup> showed that certain salts have abnormally high molecular weights in acetone solutions, although the same solutions conduct the electric current to a considerable extent. He pointed out the fact that this is not inconsistent with Arrhenius's theory of electrolytic dissociation, since it is quite conceivable that association and dissociation may occur in the same solution. It may be remarked that this is known to be the case, for instance, with many homogeneous liquids, such as water. The salts examined by Jones and found to have molecular weights above the normal, were cadmium iodide and ammonium sulphocyanate, both of which Dutoit and Friderich<sup>2</sup> had previously described as having normal molecular weights in acetone. If the above-noted abnormal conductivities are to be explained by assuming association of the electrolyte, it should be possible, by attaining sufficiently

<sup>1</sup>Amer. Chem. Jour., 27, 16 (1902).<sup>2</sup>Bull. Soc. Chim. [3], 19, 324 (1896).

great dilution, to break down these associated molecules into single molecules, and subsequently into ions; in which case the molecular conductivity might reach a value in accord with the rule that has been established in practically all other cases that have been tested, namely, that molecular conductivity is inversely proportional to viscosity. The curves representing molecular conductivity and fluidity, respectively, would then assume similar forms, minima in the one corresponding to minima in the other, etc.

An effort has been made to determine the conductivities of the solutions in question at high dilutions, approaching the region of complete dissociation. We can see no reason why there should be any constant relation between molecular conductivities and viscosity in different solvents until this point is reached, bearing in mind the widely differing degrees of dissociation existing in solutions of the same concentration in different solvents. In very dilute solutions the difference between the viscosity of the solution and that of the solvent is generally much less than the experimental error, hence we have directly compared our values for the conductivity of the solution with those for the viscosity of the solvent.

The questions for which we have sought the answer are, then, the following:

1. Will those salts that have, at ordinary concentrations, abnormally low values for molecular conductivity possess, when completely dissociated, values which are inversely proportional to the coefficients of viscosity?
2. If so, is the product of molecular conductivity and viscosity constant for mixed solvents and at different temperatures?
3. Is the value of the constant the same for different electrolytes?
4. Are the abnormal conductivities in acetone and mixtures of acetone with other solvents due to association of the salt?

#### EXPERIMENTAL.

The determination of conductivity in very dilute solutions is attended with considerable difficulty. Dutroite and Levier,<sup>1</sup> and Dutoit,<sup>2</sup> commenting upon the lack of agreement between conductivity values in acetone as obtained by different investigators, attributed the differences chiefly to the use of platinized electrodes, to the action of light, and to the use of impure solvents. Cohen<sup>3</sup> had already noticed that electrodes which are coated with platinum black cause changes in the solutions, resulting in fictitious conductivity values; and he supposed this to be due to catalytic action of the platinum black. Dutoit and Levier showed that such electrodes gave rise to errors, through adsorption of the dissolved substance; they also observed that the action of light upon acetone solutions causes a decrease in the conductivity, this change being reversed if the solution is subsequently placed in the dark.

In working with very dilute solutions, it becomes necessary either to make comparatively large amounts of each solution by direct weighing of the electrolyte, or to obtain the highly dilute solution by successive additions of solvent to the more concentrated solutions. The first method becomes impracticable when using solvents which are relatively difficult to prepare in the pure state. The second method introduces the error due to the large number of volume measurements which are neces-

<sup>1</sup>Journ. Chim. Phys., 3, 435 (1906).

<sup>2</sup>Zeit. Elektrochem., 12, 642 (1906).

<sup>3</sup>Loc. cit.

sarily made. We have, however, followed the latter method, making each solution from the one next higher in concentration.

#### APPARATUS.

In making conductivity measurements Kohlrausch's method was used, the Wheatstone bridge, induction coil, resistance coils, and telephone being made by Leeds and Company, of Philadelphia. The resistance coils were found to be accurate to within 0.04 per cent. For high resistances, two sets of coils were placed in series, giving a total available resistance of 42,000 ohms. The bridge wire was calibrated by the method of Strouhal and Barus.<sup>1</sup> For compensating the electrostatic capacity of the conductivity cells when measuring high resistances, a condenser was used, consisting of two brass plates, sliding over each other and separated by a thin sheet of paraffined paper. The conductivity cells were those described by Jones and Bingham,<sup>2</sup> and the resistance capacity was determined by the use of 0.02 normal and 0.002 normal potassium chloride solutions, 129.7, the value given by Ostwald,<sup>3</sup> being taken as the molecular conductivity of the 0.02 normal solution. The electrodes were platinized before using, by electrolysis of a dilute solution of platinum chloride in the cell, after which they were heated in the flame of a blast-lamp until whitened. After using a given solution the cell was thoroughly washed out and allowed to stand filled with distilled water for at least a day; it was then dried by means of alcohol. We satisfied ourselves, by repeated tests, that this method of drying did not produce acid on the electrodes. Measurements were made at 0° and 25°. The thermometers were graduated in 0.2° intervals, and were compared with a thermometer that was certified by the Reichsanstalt.

Viscosity measurements were made by means of a modified form of the Ostwald viscosimeter.<sup>4</sup> The modification has been described by Jones and Veazey.<sup>5</sup> Viscosity was calculated from the formula

$$\eta = \eta_0 \cdot \frac{ST}{S_0T_0}$$

in which  $\eta$  is the viscosity coefficient for the fluid in question,  $\eta_0$  is the viscosity coefficient for water at the temperature at which the experiment is being carried out,  $S$  is the specific gravity of the solvent or solution,  $T$  is the time of flow of the solvent or solution,  $S_0$  is the specific gravity of water at the given temperature, and  $T_0$  is the time of flow for water. Fluidity was calculated from the formula

$$\text{Fluidity} = \Phi = \frac{1}{\eta}$$

The viscosity coefficients for water which were used in the calculations are those taken from the researches of Thorpe and Rodger.<sup>6</sup> Specific gravities were determined by the use of the picnometer described by Jones and Veazey. The viscosimeters and picnometers were made for us by Eimer and Amend of New York.

<sup>1</sup>Wied. Ann., 10, 326 (1880).

<sup>2</sup>Amer. Chem. Journ., 24, 493 (1906).

<sup>3</sup>Lehrbuch, 2 Aufl., S. 732.

<sup>4</sup>Physiko-Chemische Messungen, 2 Aufl., S. 259.

<sup>5</sup>Zeit. phys. Chem., 61, 641 (1906).

<sup>6</sup>Phil. Trans., 185 (A), 307 (1894).

Burettes and graduated flasks were calibrated by direct weighing of distilled water, on the basis of the true liter, and corrected to use at 20°. Pipettes were not used in any part of the work.

#### SOLVENTS.

Water was purified by the method of Jones and Mackay,<sup>1</sup> ordinary distilled water being twice redistilled from chromic acid and once from barium hydroxide. The stills and bottles were protected from the entrance of carbon dioxide by a tube of soda-lime. The average specific conductivity of the purified water was  $1.2 \times 10^{-6}$  at 0°.

Methyl alcohol was prepared by boiling over lime and subsequent distillation into a bottle containing fresh lime, where it was allowed to stand for several weeks. It was redistilled immediately before using, and its average specific conductivity was  $1 \times 10^{-6}$  at 0°.

Ethyl alcohol was prepared in the same manner as methyl alcohol. The average specific conductivity at 0° was  $5 \times 10^{-7}$ .

Acetone was allowed to stand for a month or more over fused calcium chloride, and was distilled immediately before using. Our experience with acetone was quite different from that of Dutoit,<sup>2</sup> in that we found that either acetone or solutions in acetone increased in conductivity very decidedly when exposed to sunlight or even fairly bright diffused light. After distillation, therefore, the acetone was kept in the dark except when being used. It is believed that any error due to impurities in the acetone has been small in most cases, since acetone was obtained having a specific conductivity as low as  $0.57 \times 10^{-7}$  reciprocal Siemens units at 0°, and  $0.75 \times 10^{-7}$  at 25°. Dutoit and Levier stated that Benz<sup>3</sup> obtained acetone having a specific conductivity of  $0.23 \times 10^{-7}$  reciprocal Siemens units at 18°, this being the lowest of which we have found any record.

#### SOLUTIONS.

In all cases conductivity measurements were made with solutions from solvents which were distilled on the same or the preceding day. Solvents and solutions were kept in bottles of Jena glass. In mixing solvents and in making solutions, they were placed in a 20° bath for some time before diluting to the mark on the flask. In designating mixed solvents percentage by volume is understood.

An examination of the published viscosity data for mixed solvents will show that there are slight differences between the values given by different investigators, although those given by any one person are generally consistent among themselves. It is probable that such discrepancies are caused chiefly by differences in the amount and kind of unavoidable impurities in the solvents. For this reason we have determined the viscosity of all of our solvents, and the data given in table 85 are those which have been obtained in this investigation. Figures 44 and 45 are drawn from these data.

In table 85 the symbols have the following significance:  $\eta$  0° is the coefficient of viscosity at 0°,  $\eta$  25° that at 25°,  $\Phi$  0° the fluidity at 0°, and  $\Phi$  25° that at 25°. The temperature coefficient of fluidity is the change in fluidity per degree, divided by the fluidity at 0°.

<sup>1</sup>Zeit. phys. Chem., **22**, 237 (1897).

<sup>2</sup>Lec. cit.

<sup>3</sup>Dissertation, Lausanne, 1905.

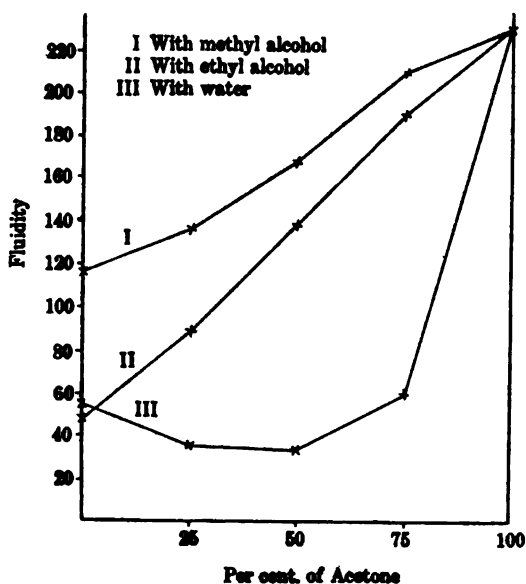


FIG. 44.—Fluidity of acetone mixtures at 0°.

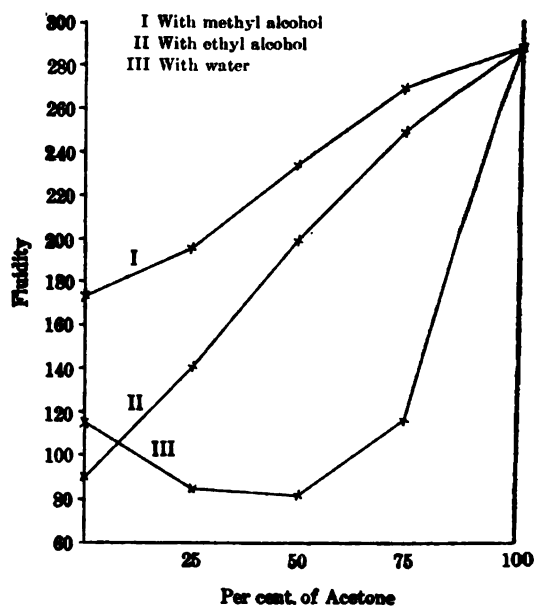


FIG. 45.—Fluidity of acetone mixtures at 25°.

## VISCOSITY AND FLUIDITY OF ACETONE MIXTURES.

Molecular conductivities are indicated in the conductivity tables, and  $V$  is the number of liters of solution containing a gram-molecule of the electrolyte. The temperature coefficient of conductivity is the change in molecular conductivity per degree, divided by the molecular conductivity at 0°.

The first compound that we studied in this connection was lithium nitrate, and the sample used was Kahlbaum's preparation, which, after testing, was dried to constant weight at 150°.

TABLE 85.—Viscosity and Fluidity of Acetone Mixtures at 0° and 25°.

	Per cent acetone.	$\eta$ 0°	$\eta$ 25°	$\Phi$ 0°	$\Phi$ 25°	Temperature coefficients.
With methyl alcohol.....	0	0.00857	0.00583	116.71	171.60	0.0176
	25	0.00734	0.00517	136.22	193.24	0.0167
	50	0.00596	0.00433	167.76	231.01	0.0151
	75	0.00471	0.00370	212.12	270.12	0.0109
	100	0.00429	0.00346	233.21	288.95	0.0096
With ethyl alcohol.....	0	0.02103	0.01180	47.56	84.74	0.0313
	25	0.01131	0.00726	88.43	137.77	0.0223
	50	0.00725	0.00506	137.92	197.48	0.0173
	75	0.00522	0.00398	191.54	251.29	0.0125
	100	0.00429	0.00346	233.21	288.95	0.0096
With water.....	0	0.01778	0.00891	56.24	112.30	0.0399
	25	0.02908	0.01250	34.38	79.89	0.0529
	50	0.03005	0.01305	33.28	76.63	0.0521
	75	0.01659	0.00885	60.29	112.97	0.0349
	100	0.00429	0.00346	233.21	288.95	0.0096

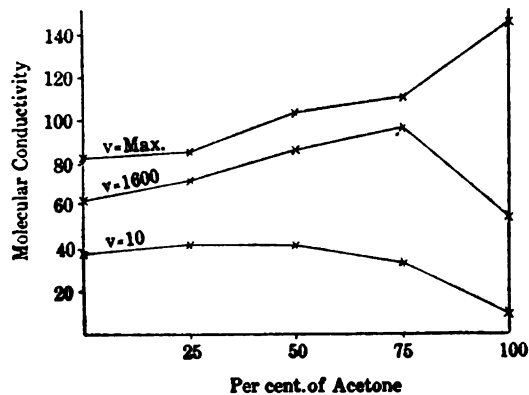


FIG. 46.—Conductivity of lithium nitrate in mixtures of acetone and methyl alcohol at 0°.

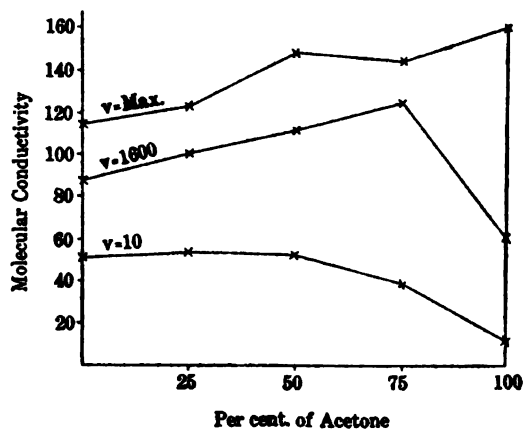


FIG. 47.—Conductivity of lithium nitrate in mixtures of acetone and methyl alcohol at 25°.

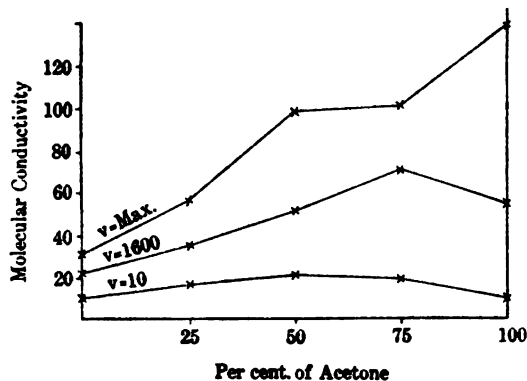


FIG. 48.—Conductivity of lithium nitrate in mixtures of acetone and ethyl alcohol at 0°.

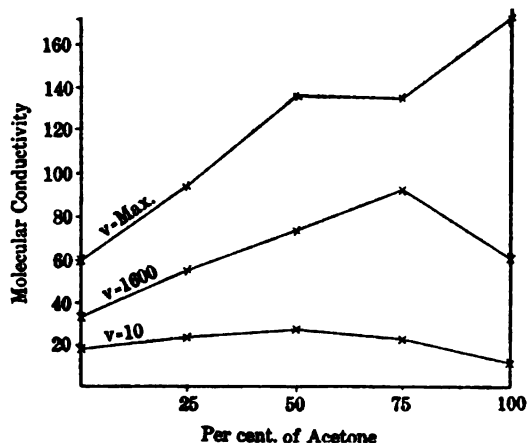


FIG. 49.—Conductivity of lithium nitrate in mixtures of acetone and ethyl alcohol at 25°.

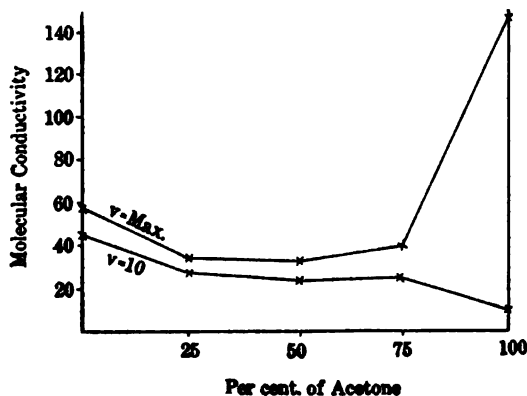


FIG. 50.—Conductivity of lithium nitrate in mixtures of acetone and water at 0°.

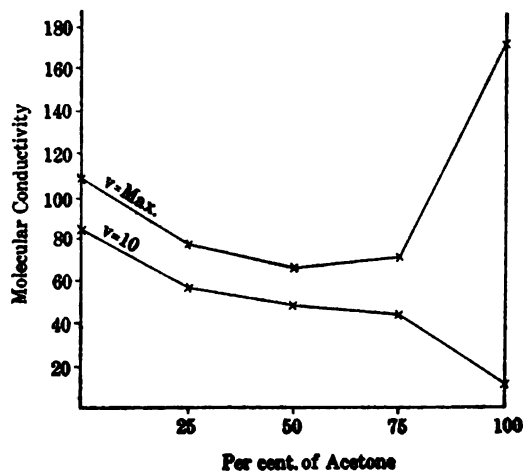


FIG. 51.—Conductivity of lithium nitrate in mixtures of acetone and water at 25°.



The conductivity of lithium nitrate in mixtures of acetone with methyl alcohol, ethyl alcohol, and water, respectively, was determined by Jones and Bingham,<sup>1</sup> using solutions whose concentration varied from  $V=10$  to  $V=1,600$ . The results are as already indicated, namely, that the form of the curves representing molecular conductivity for different percentages of acetone was different from that of the fluidity curves, in that conductivities in acetone were decidedly less than normal, and that no known dilution law would apply to the more concentrated solutions. We have used the same solvents and mixtures of solvents, and have measured the conductivities at dilutions as high as was possible with any fair degree of accuracy, considering the conductivity of the solvent. The results are shown in tables 86 to 89 and in figs. 46 to 51, inclusive. In the figures, the curves for  $V=10$  and  $V=1,600$  are drawn from the data of Jones and Bingham, and are given here in order to show the abnormality produced by acetone as a solvent, and the striking change in the conductivity as the dilution increases.

TABLE 86.—*Conductivity of Lithium Nitrate in Mixtures of Acetone and Methyl Alcohol.*

V	At 0°, per cent acetone.					At 25°, per cent acetone.				
	0 p.ct.	25 p.ct.	50 p.ct.	75 p.ct.	100 p.ct.	0 p.ct.	25 p.ct.	50 p.ct.	75 p.ct.	100 p.ct.
2,500	63.4	69.6	87.0	96.8	61.0	88.6	97.2	122.7	124.5	65.9
5,000	66.1	71.8	91.5	101.5	76.9	92.5	100.1	132.5	131.1	85.7
10,000	68.1	78.8	99.4	103.5	94.1	94.3	107.9	144.0	133.7	105.1
30,000	81.6	84.3	103.0	110.9	.....	113.2	121.5	138.0	142.6	.....
50,000	83.0	83.8	.....	.....	129.8	114.0	114.5	.....	.....	153.6
100,000	.....	.....	.....	.....	146.5	.....	.....	.....	.....	171.8

TABLE 87.—*Conductivity of Lithium Nitrate in Mixtures of Acetone and Ethyl Alcohol.*

V	At 0°, per cent acetone.					At 25°, per cent acetone.				
	0 p.ct.	25 p.ct.	50 p.ct.	75 p.ct.	100 p.ct.	0 p.ct.	25 p.ct.	50 p.ct.	75 p.ct.	100 p.ct.
2,500	22.2	35.9	53.0	.....	61.0	37.4	55.5	74.5	97.3	65.9
5,000	22.7	38.0	56.1	79.8	76.9	38.3	58.1	79.3	105.2	85.7
10,000	24.1	38.7	57.3	81.6	94.1	40.0	59.4	83.3	109.0	105.1
30,000	28.1	.....	.....	80.6	.....	48.0	.....	.....	106.5	.....
50,000	27.2	43.4	64.9	79.7	129.8	44.7	68.5	93.4	112.8	153.6
100,000	32.0	55.0	71.9	100.0	146.5	60.1	93.0	105.1	135.4	171.8
200,000	.....	.....	99.3	.....	.....	.....	.....	136.1	.....	.....

TABLE 88.—*Conductivity of Lithium Nitrate in Mixtures of Acetone and Water.*

V	At 0°, per cent acetone.					At 25°, per cent acetone.				
	0 p.ct.	25 p.ct.	50 p.ct.	75 p.ct.	100 p.ct.	0 p.ct.	25 p.ct.	50 p.ct.	75 p.ct.	100 p.ct.
2,500	56.9	34.1	29.9	37.2	61.0	104.6	73.4	61.6	66.7	65.9
5,000	58.4	34.2	31.4	37.6	76.9	108.3	74.7	64.4	69.3	85.7
10,000	58.5	33.5	31.8	38.7	94.1	108.7	76.3	64.8	69.6	105.1
50,000	.....	.....	.....	.....	129.8	.....	.....	.....	.....	153.6
100,000	.....	.....	.....	.....	146.5	.....	.....	.....	.....	171.8

<sup>1</sup>*Loc. cit.*

TABLE 89.—*Temperature Coefficients of Conductivity of Lithium Nitrate.*

	Per cent acetone.					
	V	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
In acetone and methyl alcohol.	2,500	0.0159	0.0159	0.0164	0.0115	0.0032
	5,000	0.0159	0.0157	0.0179	0.0116	0.0046
	10,000	0.0153	0.0147	0.0182	0.0117	0.0047
	30,000	0.0155	0.0176	0.0136	0.0114	.....
	50,000	0.0149	0.0146	.....	.....	0.0073
	100,000	.....	.....	.....	.....	0.0070
In acetone and ethyl alcohol....	2,500	0.0274	0.0218	0.0162	.....	0.0032
	5,000	0.0275	0.0212	0.0166	0.0127	0.0046
	10,000	0.0264	0.0205	0.0181	0.0134	0.0047
	30,000	0.0283	.....	.....	0.0128	.....
	50,000	0.0257	0.0231	0.0175	0.0161	0.0073
	100,000	0.0351	0.0276	0.0184	0.0142	0.0070
In acetone and water.....	2,500	0.0335	0.0461	0.0426	0.0317	0.0032
	5,000	0.0342	0.0473	0.0420	0.0337	0.0046
	10,000	0.0343	0.0511	0.0415	0.0319	0.0047

In the solutions in pure water and in pure acetone it would seem that complete dissociation has been very nearly attained. In aqueous solution the value for  $\mu_{\infty}$  at 18°, calculated from the law of Kohlrausch and by use of the constants for the ions of lithium nitrate as given by him,<sup>1</sup> is 95. The corresponding value, calculated from our highest conductivity at 0°, by use of the temperature coefficient, is 94. In the solutions other than in water and acetone, complete dissociation has not been reached, but we have approached it closely enough so that the properties of the completely dissociated solution may be predicted. The conductivity curves have assumed nearly the same form as the fluidity curves for the solvents.

In order to test the applicability of Ostwald's dilution law, the values of  $K = \frac{a^3}{(1-a)\nu}$  have been calculated for the solutions of lithium nitrate in acetone from all available data. In table 90 the values for  $\mu_{\infty}$  from  $V=10$  to  $V=1,600$ , inclusive, are taken from the paper of Jones and Bingham. From this point the values are those which have been obtained in this investigation.

TABLE 90.—*Ionization Constant for Lithium Nitrate in Acetone.*

V	At 0°.			V	At 25°.		
	$K \times 10^3$	V	$K \times 10^3$		$K \times 10^3$	V	$K \times 10^3$
10	0.541	1,600	0.168	10	0.670	1,600	0.130
50	0.235	2,500	0.120	50	0.195	2,500	0.096
100	0.198	5,000	0.117	100	0.156	5,000	0.098
200	0.186	10,000	0.116	200	0.134	10,000	0.096
400	0.165	50,000	0.145	400	0.115	50,000	0.147
800	0.179	.....	.....	800	0.126	.....	.....

It will be seen that  $K$  becomes practically constant at  $V=200$  for solutions at both 0° and 25°, which would indicate that the highest value for  $\mu_{\infty}$ , that obtained at  $V=100,000$ , is not far from the maximum molecular conductivity. The fact

<sup>1</sup>Sitzungsber. d. K. Preuss. Akad. d. Wiss. Math. Kl. 1904, 574 u. 583.

that  $K$  decreases rapidly at first may be explained on the general ground that Ostwald's dilution law is not applicable to solutions of strong electrolytes, or upon the assumption of polymerization of the electrolyte. It will appear later that there is reason for the latter view.

TABLE 91.— $\eta \cdot \mu$ , for Lithium Nitrate in Mixed Solvents.

	Per cent acetone.	$\mu$ , 0°	$\eta$ 0°	$\eta \cdot \mu$	$\mu$ , 25°	$\eta$ 25°	$\eta \cdot \mu$
In acetone and methyl alcohol.	0	83	0.0086	0.69	114	0.0058	0.65
	25	84	0.0073	0.61	122	0.0052	0.63
	50	103	0.0060	0.62	144	0.0043	0.62
	75	111	0.0047	0.52	143	0.0037	0.53
	100	146	0.0043	0.63	172	0.0035	0.60
In acetone and ethyl alcohol..	0	32	0.0210	0.67	60	0.0118	0.71
	25	55	0.0113	0.62	93	0.0073	0.71
	50	100	0.0072	0.72	136	0.0051	0.69
	75	100	0.0052	0.52	135	0.0040	0.54
	100	146	0.0043	0.63	172	0.0035	0.60
In acetone and water.....	0	58	0.0178	1.03	108	0.0069	0.96
	25	34	0.0291	0.99	76	0.0125	0.95
	50	32	0.0300	0.96	65	0.0131	0.85
	75	39	0.0166	0.65	70	0.0088	0.62
	100	146	0.0043	0.63	172	0.0035	0.60

In table 91 is given the calculated product of viscosity and molecular conductivity for all of the solutions. In these calculations we have used, in each case, the viscosity of the solvent, which is practically identical with that of the dilute solution, and have taken for  $\mu$ , the highest value which has been obtained in this work.

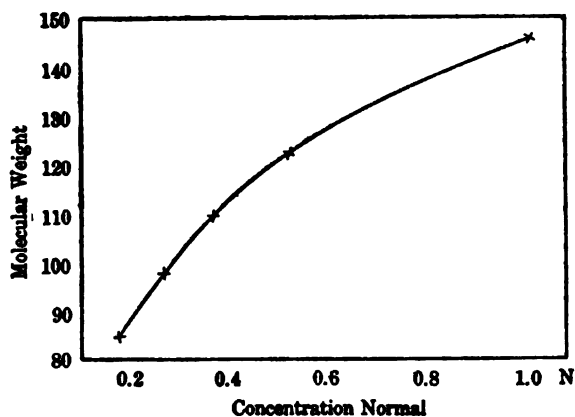


FIG. 52.—Molecular weight of lithium nitrate in acetone.

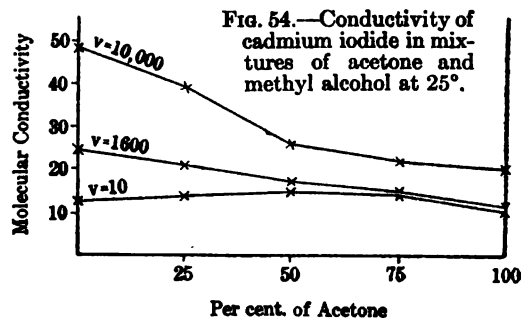
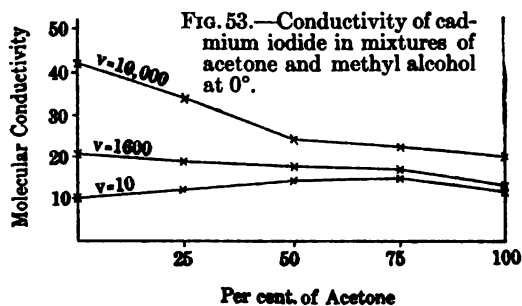
The product of viscosity and molecular conductivity is seen to be nearly a constant for mixtures of acetone with methyl alcohol and with ethyl alcohol. This constant is independent of temperature, and its value is nearly 0.70, the value found by Walden for tetraethylammonium iodide in a large number of organic solvents. For mixtures of acetone with water the product varies between about 1.00, the value for water, and about 0.60, that for acetone. The product for water is also shown to

be the same as Walden's constant for aqueous solutions. It is probable that, if complete dissociation could have been obtained in acetone, the product for this solution would have been found to be nearly 0.70, and that the product for mixtures of acetone and water would conform to the rule of mixtures. We have no explanation to offer for the fact that water differs so strikingly from the organic solvents with respect to the numerical value of the product of maximum molecular conductivity and viscosity.

TABLE 92.—*Molecular Weight of Lithium Nitrate in Acetone.*

Acetone.	LiNO <sub>3</sub> .	Concentration, normal.	B. P. rise.	Molecular weight.
<i>grams</i>	<i>grams</i>		<i>°C.</i>	
58.07	0.3625	0.09	0.130	83.1
52.74	0.7076	0.19	0.233	99.3
49.99	1.0640	0.30	0.326	112.6
46.30	2.2033	0.48	0.451	127.1
54.35	3.9229	1.05	0.805	154.7

In order to test the assumption that the low conductivity shown by ordinary solutions of lithium nitrate in acetone is due to association of the salt, the molecular weight of lithium nitrate in acetone was determined by the boiling-point method. The apparatus used was that designed by Jones,<sup>1</sup> the thermometer being the Beckmann instrument, graduated to 0.01°. The boiling-point constant for acetone was taken as 17.25, which is that found in a redetermination by Jones.<sup>2</sup> The usual corrections were made for changes in barometric pressure. The results are shown in table 92, and the molecular weights are plotted against concentrations in fig. 53.



The normal molecular weight of lithium nitrate is 69.07. The fact that, even in the most dilute solution which could be used with accuracy (0.09 N.), the molecular weight is greater than this number, is significant. If it be remembered that a portion of the salt is also ionized, and that the molecular weight as obtained by the boiling-point method is the average weight of associated molecules, single molecules, and ions, existing simultaneously in the solution, it will readily be surmised that there must be a certain degree of association at much greater dilutions. This would explain the departure from the dilution law in those solutions in which the association has not entirely disappeared.

It has already been stated that cadmium iodide was found by Jones to be associated when dissolved in acetone. We have studied the conductivity of cadmium

<sup>1</sup>Amer. Chem Jour

581(1897); Zeit. phys. Chem., 31, 119 (1899).

<sup>2</sup>Ibid., 27, 16 (1902).

iodide in acetone and in binary mixtures containing acetone, in order to determine whether such solutions are analogous to those of lithium nitrate, as they should be if the proposed explanation of the peculiar behavior of the latter is correct. The results of the conductivity measurements are shown in tables 92 to 97 and in figs. 53 to 58, inclusive.

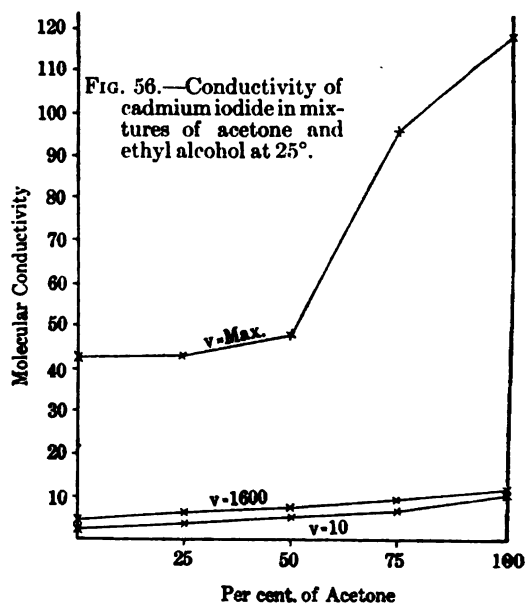
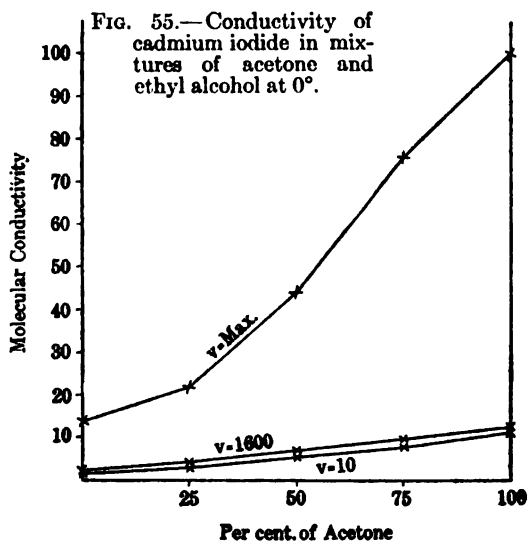


Fig. 57.—Conductivity of cadmium iodide in mixtures of acetone and water at 0°.

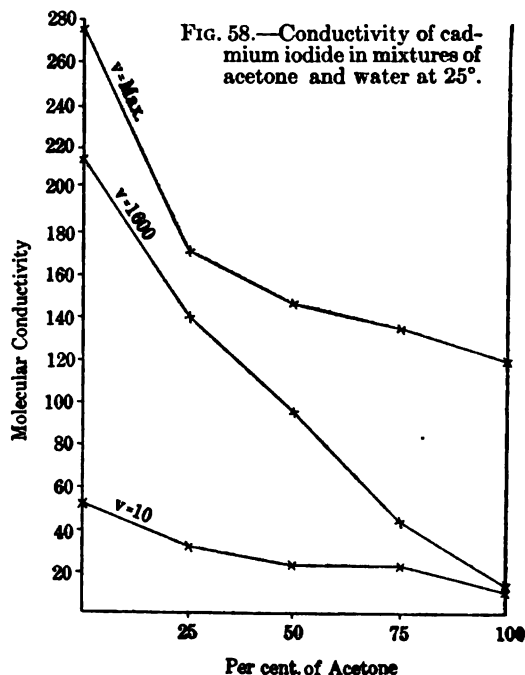
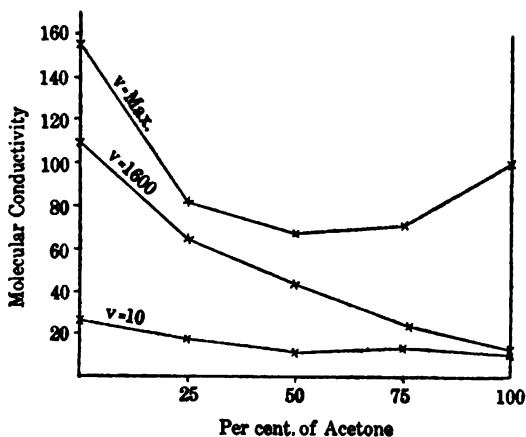


TABLE 93.—*Conductivity of Cadmium Iodide in Mixtures of Acetone and Methyl Alcohol at 0° and 25°.*

V	Per cent acetone, at 0°.					Per cent acetone, at 25°.				
	0 p.ct.	25 p.ct.	50 p.ct.	75 p.ct.	100 p.ct.	0 p.ct.	25 p.ct.	50 p.ct.	75 p.ct.	100 p.ct.
10	10.31	12.39	14.31	15.13	11.56	12.42	14.03	15.11	14.68	10.29
50	11.72	13.94	15.63	16.36	12.10	13.66	15.16	15.75	15.19	10.15
100	12.34	14.35	15.89	16.47	11.88	14.28	15.46	16.10	14.96	9.92
200	13.01	14.44	15.83	16.48	12.22	15.03	15.53	15.66	14.84	10.34
400	14.92	15.56	16.62	16.89	12.11	17.42	16.59	16.18	15.18	10.23
800	17.42	16.86	17.05	16.90	12.63	20.36	18.18	16.76	14.98	10.88
1,600	20.83	18.77	17.37	17.00	12.87	24.53	20.76	17.32	14.98	11.16
2,500	25.60	21.09	18.13	17.19	12.27	28.95	24.18	18.14	15.08	11.64
5,000	33.12	27.05	21.2	20.64	15.35	40.0	32.4	21.7	19.1	13.91
10,000	41.5	33.4	24.2	22.2	19.53	49.2	39.8	25.9	21.7	20.5
30,000	46.8	48.0	32.2	29.3	29.4	54.2	56.6	33.1	27.6	32.8
50,000	55.0	60.8	39.2	32.3	37.5	55.9	80.6	43.3	28.9	45.4
100,000	62.7	94.3	.....	.....	78.0	63.0	105.5	.....	.....	78.6
200,000	.....	.....	.....	.....	93.0	.....	.....	.....	.....	113.0
400,000	.....	.....	.....	.....	100.0	.....	.....	.....	.....	118.0

TABLE 94.—*Temperature Coefficients of Conductivity of Cadmium Iodide in Mixtures of Acetone and Methyl Alcohol.*

V	Per cent acetone.				
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
10	0.0082	0.0051	+0.0022	-0.0011	-0.0045
50	0.0066	0.0038	+0.0003	-0.0030	-0.0063
100	0.0063	0.0031	+0.0005	-0.0036	-0.0064
200	0.0062	0.0031	-0.0003	-0.0039	-0.0061
400	0.0067	0.0026	-0.0009	-0.0040	-0.0062
800	0.0066	0.0031	-0.0007	-0.0045	-0.0054
1,600	0.0071	0.0064	-0.0001	-0.0047	-0.0053
2,500	0.0052	0.0059	0.0000	-0.0049	-0.0023
5,000	0.0083	0.0078	+0.0009	-0.0030	-0.0039
10,000	0.0074	0.0077	+0.0028	-0.0009	+0.0021
30,000	0.0063	0.0072	+0.0011	-0.0023	+0.0046
50,000	0.0006	0.0130	+0.0042	-0.0042	+0.0084
100,000	0.0002	0.0047	.....	.....	+0.0066
200,000	.....	.....	.....	.....	+0.0086
400,000	.....	.....	.....	.....	+0.0072

TABLE 95.—*Conductivity of Cadmium Iodide in Mixtures of Acetone and Ethyl Alcohol at 0° and 25°.*

V	Per cent acetone, at 0°.					Per cent acetone, at 25°.				
	0 p.ct.	25 p.ct.	50 p.ct.	75 p.ct.	100 p.ct.	0 p.ct.	25 p.ct.	50 p.ct.	75 p.ct.	100 p.ct.
10	1.69	3.43	5.58	8.15	11.56	2.11	3.54	5.19	7.03	10.29
50	1.62	3.37	5.51	7.97	12.10	2.00	3.40	4.91	6.58	10.15
100	1.60	3.42	5.52	7.92	11.88	2.03	3.45	4.95	6.58	9.92
200	1.67	3.49	5.63	7.98	12.22	2.16	3.61	4.97	6.65	10.34
400	1.74	3.54	5.86	8.16	12.11	2.42	3.87	5.53	6.95	10.23
800	1.93	4.11	6.38	8.57	12.63	2.97	4.78	6.27	6.48	10.88
1,600	2.31	4.63	7.20	10.01	12.87	4.02	5.93	7.70	9.62	11.16
2,500	2.28	5.42	9.41	10.52	12.27	4.75	7.58	11.10	10.64	11.64
5,000	4.6	7.0	13.0	13.2	15.4	9.33	11.0	17.1	15.5	13.9
10,000	7.8	8.4	16.0	21.8	19.5	15.2	14.3	21.5	26.0	20.5
25,000	.....	15.1	26.5	29.4	.....	.....	15.0	34.5	35.3	.....
50,000	13.9	22.0	43.6	6.0	37.5	41.7	43.1	58.3	75.0	45.4
100,000	10.4	.....	.....	76.0	78.0	42.0	.....	.....	96.0	78.6
200,000	.....	.....	.....	.....	93.0	.....	.....	.....	.....	113.0
400,000	.....	.....	.....	.....	100.0	.....	.....	.....	.....	118.0

TABLE 96.—*Temperature Coefficients of Conductivity of Cadmium Iodide in Mixtures of Acetone and Ethyl Alcohol.*

V	Per cent acetone.				
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
10	0.0099	0.0013	−0.0028	−0.0055	−0.0045
50	0.0094	0.0004	−0.0044	−0.0070	−0.0063
100	0.0107	0.0004	−0.0041	−0.0067	−0.0064
200	0.0118	0.0014	−0.0047	−0.0066	−0.0061
400	0.0156	0.0037	−0.0023	−0.0059	−0.0062
800	0.0215	0.0065	−0.0007	−0.0097	−0.0054
1,600	0.0296	0.0112	+0.0028	−0.0016	−0.0053
2,500	0.0433	0.0157	+0.0072	+0.0005	−0.0023
5,000	0.0413	0.0231	+0.0127	+0.0069	−0.0039
10,000	0.0379	0.0282	+0.0138	+0.0077	+0.0021
25,000	.....	0.0262	+0.0120	+0.0080	.....
50,000	0.0800	0.0384	+0.0135	+0.0100	+0.0084
100,000	0.1230	.....	.....	+0.0105	+0.0066
200,000	.....	.....	.....	.....	+0.0086
400,000	.....	.....	.....	.....	+0.0072

TABLE 97.—*Conductivity of Cadmium Iodide in Mixtures in Acetone and Water at 0° and 25°.*

V	Per cent acetone, at 0°.					Per cent acetone, at 25°.				
	0 p.ct.	25 p.ct.	50 p.ct.	75 p.ct.	100 p.ct.	0 p.ct.	25 p.ct.	50 p.ct.	75 p.ct.	100 p.ct.
10	25.95	15.00	11.40	14.17	11.56	52.68	30.65	21.90	23.08	10.29
50	45.88	22.49	13.40	15.45	12.10	95.43	49.94	27.12	24.83	10.15
100	58.16	29.26	15.39	16.12	11.88	119.95	65.65	32.46	25.98	9.92
200	70.6	38.13	19.00	17.01	12.22	144.4	85.73	41.4	27.77	10.34
400	83.0	47.6	24.4	18.2	12.11	167.8	105.6	54.5	30.14	10.23
800	96.3	56.4	33.0	20.6	12.63	191.6	124.5	73.1	34.81	10.88
1,600	110.7	63.9	43.3	24.6	12.87	215.8	139.7	95.0	43.16	11.16
2,500	116.1	66.2	49.3	27.8	12.27	225.4	145.6	105.8	49.7	11.64
5,000	126.2	72.4	57.2	35.6	15.4	240.2	155.1	122.1	66.9	13.9
10,000	140.6	80.8	63.8	48.3	19.5	261.2	170.6	135.2	91.0	20.5
25,000	155.2	.....	67.2	62.1	.....	278.8	.....	144.2	117.0	.....
50,000	.....	.....	.....	71.0	37.5	.....	.....	.....	134.0	45.4
100,000	.....	.....	.....	.....	78.0	.....	.....	.....	.....	78.6
200,000	.....	.....	.....	.....	93.0	.....	.....	.....	.....	113.0
400,000	.....	.....	.....	.....	100.0	.....	.....	.....	.....	118.0

TABLE 98.—*Temperature Coefficients of Conductivity of Cadmium Iodide in Mixtures of Acetone and Water.*

V	Per cent acetone.				
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
10	0.0402	0.0417	0.0369	0.0251	−0.0045
50	0.0432	0.0488	0.0409	0.0243	−0.0063
100	0.0424	0.0484	0.0443	0.0238	−0.0064
200	0.0418	0.0499	0.0471	0.0263	−0.0061
400	0.0409	0.0487	0.0493	0.0261	−0.0062
800	0.0398	0.0412	0.0486	0.0275	−0.0054
1,600	0.0385	0.0474	0.0477	0.0302	−0.0053
2,500	0.0376	0.0479	0.0458	0.0315	−0.0023
5,000	0.0361	0.0456	0.0454	0.0352	−0.0039
10,000	0.0343	0.0444	0.0447	0.0353	+0.0021
25,000	0.0319	.....	0.0458	0.0355	.....
50,000	.....	.....	.....	0.0357	+0.0084
100,000	.....	.....	.....	.....	+0.0066
200,000	.....	.....	.....	.....	+0.0086
400,000	.....	.....	.....	.....	+0.0072

The conductivity of cadmium iodide in water has been studied by Lenz,<sup>1</sup> Grotrian,<sup>2</sup> Wershoven,<sup>3</sup> Zelinski and Krapiwinski,<sup>4</sup> Fox,<sup>5</sup> and Jones and Lindsay.<sup>6</sup> Hittorf<sup>7</sup> determined the apparent transport numbers of the anion in solutions of different concentrations, and concluded that in the more concentrated solutions double molecules exist, which dissociate to  $\text{Cd}^{++}$  and  $\text{CdI}_4^{-}$ . Lenz also believed that the more concentrated solutions contain complex anions. McBain,<sup>8</sup> on the other hand, followed a different line of argument and decided that double molecules exist, but that they dissociate to form the ions  $\text{Cd}^{++}$  and  $2\text{CdI}_3^{-}$ . The conclusion was reached that at greater dilutions these ions are also broken down into the simpler ions  $\text{Cd}^{++}$  and  $3\text{I}^{-}$ , resulting in a large increase in the molecular conductivity.

Bein<sup>9</sup> also studied the transport numbers of the anion of cadmium iodide at different temperatures, and showed that there is no perceptible change between 20° and 75°.

From the work of Kummel<sup>10</sup> it is evident that the apparent transport numbers of the halogens reach their minimum values in solutions of the cadmium halides which vary in concentration from 0.01 normal to 0.002 normal. Since the abnormally large apparent transport number for the halogen is supposed to be due to the fact that cadmium migrates towards both electrodes, this accords with the idea held by Hittorf, Lenz, and McBain, that the complex anions break down with increasing dilution.

TABLE 99.—Ionization Constant for Cadmium Iodide in Water.

V	At 0°.			At 25°.			
	$K \times 10^3$ .	V	$K \times 10^3$ .	V	$K \times 10^3$ .	V	$K \times 10^3$ .
10	0.338	800	0.126	10	0.425	800	0.189
50	0.257	1,600	0.108	50	0.352	1,600	0.166
100	0.223	2,500	0.089	100	0.324	2,500	0.134
200	0.194	5,000	0.071	200	0.275	5,000	0.106
400	0.190	10,000	0.092	400	0.228	10,000	0.136

Herz and Lewy<sup>11</sup> carried out partition experiments with cadmium iodide in water and amyl alcohol, from the results of which they were led to conclude that complex ions are present in the aqueous solution.

It is not believed that the highest values for molecular conductivity which have been obtained in the present work are, in any of the solutions except those in water, the ones corresponding to complete dissociation. McBain attributed to Zelinsky and Krapiwinski the most accurate work on the conductivity of aqueous solutions of cadmium iodide, and he regarded 278, a value calculated from their results obtained at 18°, as the correct value for the maximum molecular conductivity at 25°. This corresponds with the results of our measurements, which gave 279 at 25°. It is evident, from an inspection of the values of  $K$  calculated from Ostwald's dilution law, that this is very close to the maximum molecular conductivity. The regular decrease in the value of  $K$  until the dilution reaches about 0.001 normal may be

<sup>1</sup>Mem. de St. Petersburg. [7]30, 64 (1882).<sup>2</sup>Wied. Ann., 18, 190 (1883).<sup>3</sup>Zeit. phys. Chem., 5, 481 (1890).<sup>4</sup>Ibid., 21, 35 (1896).<sup>5</sup>Ibid., 41, 458 (1902).<sup>6</sup>Amer. Chem. Journ., 28, 329 (1902).<sup>7</sup>Pogg. Ann., 106, 513 (1859).<sup>8</sup>Zeit. Elektrochem., 11, 215 (1905).<sup>9</sup>Wied. Ann., 46, 29 (1892).<sup>10</sup>Ibid., 64, 655 (1898).<sup>11</sup>Jahresber. Schles. Ges. f. vaterländ. Kultur, 1896, Naturw. Sekt., 1-9.



attributed to the non-applicability of the dilution law of Ostwald to solutions of cadmium iodide; or may be explained by the assumption of molecular association and simple ionization, or of association accompanied by the formation of complex ions, the latter being the most probable cause.

The result of the work upon the molecular conductivity of cadmium iodide in acetone shows a close analogy to the case of lithium nitrate. There is almost no change in molecular conductivity with dilution, until a concentration of 0.0002 normal is reached. From this point the increase is quite rapid, but it has not been found possible to reach the maximum molecular conductivity, though this point has been, we believe, closely approached. The Ostwald constant, calculated for these solutions, shows a very rapid decrease until  $V=5,000$ , where it is constant until  $V=50,000$ . From this point it increases quite rapidly. The large initial value of  $K$ , with its subsequent decrease, is probably due to association of the salt. The later rise in the value of  $K$  is, no doubt, due to the fact that dissociation is not complete at  $V=400,000$ , so that we have used too small a value for  $\mu_{\infty}$  in the calculation of the dissociation at greater concentrations.

TABLE 100.—*Ionization Constant for Cadmium Iodide in Acetone.*

V	At 0°.			V	At 25°.		
	$K \times 10^3$	V	$K \times 10^3$		$K \times 10^3$	V	$K \times 10^3$
10	1.60	2,500	0.007	10	0.834	2,500	0.005
50	0.33	5,000	0.005	50	0.164	5,000	0.003
100	0.16	10,000	0.005	100	0.078	10,000	0.004
200	0.08	30,000	0.004	200	0.042	30,000	0.004
400	0.041	50,000	0.005	400	0.021	50,000	0.005
800	0.012	100,000	0.028	800	0.011	100,000	0.014
1,600	0.012	200,000	0.062	1,600	0.006	200,000	0.108

It is thus evident that in acetone the dissociation is not complete at either temperature, although it is more nearly so at 0° than at 25°. This is to be expected from a knowledge of the temperature coefficient, which is negative below a dilution of 10,000 liters and has a very small positive value at higher dilutions. Since the change in conductivity, corresponding to a given rise in temperature, is the resultant of two factors which are probably opposite in their effect, *i. e.*, decrease in viscosity and probable decrease in ionization, it is seen that there must be a very large decrease in the ionization of cadmium iodide in acetone as we pass from 0° to 25°. Thus, the molecular conductivity curve for cadmium iodide in acetone-water mixtures at 0° suggests the fluidity curve for the solvents, more plainly than at 25°, and it seems probable that, could the conductivity be accurately measured at dilutions as high as 600,000 or 700,000 liters, the curves of molecular conductivity would become similar to those of fluidity, so that molecular conductivity and viscosity would be inversely proportional, as is the case with lithium nitrate and most other electrolytes. There is no means of knowing what the numerical value of the product of viscosity and conductivity would be. Taking the highest conductivity that was obtained in each case, the product is irregular, as is seen in table 101.

The irregularity in the value of the product of maximum conductivity and viscosity, in the case of acetone and methyl alcohol mixtures, is probably due to the fact that complete dissociation was more nearly approached in some cases than in others. The values for pure acetone and for pure methyl alcohol are, however, nearly the same; and we may expect that the curves for maximum molecular conductivity, when finally obtained, will be found to be nearly straight lines, similar to the fluidity curves for the solvents.

TABLE 101.— $\eta \cdot \mu_{\infty}$  for Cadmium Iodide in Mixed Solvents.

	Per cent acetone.	$\mu_{\infty} 0^{\circ}$	$\eta 0^{\circ}$	$\eta \cdot \mu_{\infty}$	$\mu_{\infty} 25^{\circ}$	$\eta 25^{\circ}$	$\eta \cdot \mu_{\infty}$
In acetone and methyl alcohol.	0	63	0.0086	0.54	63	0.0058	0.36
	25	94	0.0073	0.69	105	0.0052	0.54
	50	39	0.0060	0.23	43	0.0043	0.19
	75	32	0.0047	0.15	29	0.0037	0.11
	100	100	0.0043	0.43	118	0.0035	0.41
In acetone and ethyl alcohol.	0	14	0.0210	0.29	42	0.0118	0.50
	25	22	0.0113	0.25	43	0.0073	0.31
	50	44	0.0073	0.32	58	0.0051	0.30
	75	76	0.0052	0.40	96	0.0040	0.38
	100	100	0.0043	0.43	118	0.0035	0.41
In acetone and water.....	0	155	0.0178	2.76	279	0.0089	2.48
	25	81	0.0291	2.36	171	0.0125	2.14
	50	67	0.0301	2.02	144	0.0131	1.89
	70	71	0.0166	1.18	134	0.0088	1.18
	105	100	0.0043	0.43	118	0.0035	0.41

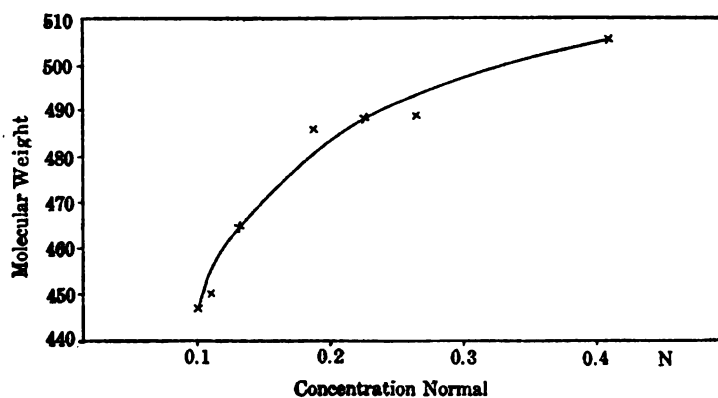


FIG. 59.—Molecular weight of cadmium iodide in acetone.

In the acetone and ethyl alcohol mixtures there is a fair degree of constancy in the product, and the conductivity curve is nearly the theoretical one. The acetone and water curve is also nearly the same as the fluidity curve for the solvents, and the value of the product almost exactly follows the rule of mixtures, although here again the exceptionally high value of the product for water is noticed, it being about 2.5 instead of 1.0, as in the case of lithium nitrate and tetraethylammonium iodide. The reason for this interesting fact must, for the present, remain unexplained.

The results obtained by Jones for the molecular weight of cadmium iodide in acetone are given in table 102 and are shown graphically in fig. 59. The molecular weight is 364, while the molecular weight found in a 0.09 normal solution in acetone is 448. Considerable polymerization is thus indicated.

TABLE 102.—*Molecular Weight of Cadmium Iodide in Acetone.*

Acetone.	CdI <sub>2</sub>	Concentration, normal.	B. P. rise.	Molecular weight.
<i>grams.</i>	<i>grams.</i>		<i>°C.</i>	
55.16	1.7789	0.09	0.124	448.6
56.03	2.0540	0.10	0.140	451.7
57.51	2.4951	0.12	0.160	467.8
56.37	3.7790	0.18	0.236	490.1
55.92	4.5020	0.22	0.282	492.4
57.28	5.4000	0.26	0.330	492.9
57.28	8.5460	0.41	0.504	510.7

#### SUMMARY.

The work of others has shown that the general law which correlates conductivity and viscosity fails in the case of lithium nitrate, lithium bromide, cobalt chloride, and calcium nitrate, when dissolved in mixtures containing acetone as one of the components of a binary solvent mixture. This is made evident by the abnormally low values for conductivity of these substances in acetone, and it was thought that it might be due to association of the salt in acetone. Determination of conductivity at high dilutions has shown that lithium nitrate, when completely dissociated, is no exception to the rule that molecular conductivity varies inversely as the viscosity; and boiling-point measurements have shown that, at ordinary concentrations, the salt is associated in acetone to a considerable extent.

Cadmium iodide had already been found to be associated in acetone, and further work on its conductivity in mixed solvents has shown that its behavior is similar to that of lithium nitrate.

The temperature coefficients of conductivity of lithium nitrate are of about the same order of magnitude as the temperature coefficients of fluidity, though generally somewhat smaller, except at high dilutions. This might be expected from the fact that dissociation is less at 25° than at 0°. This influence of temperature is seen more clearly in acetone solutions of cadmium iodide, which have negative temperature coefficients of conductivity below a dilution of 0.0001 normal.

Similar investigations are in progress, having to do with solutions of the other salts mentioned above.

## WORK OF M. R. SCHMIDT.

We have seen that certain definite relations exist between the conductivity of various electrolytes dissolved in binary mixtures of several solvents and the viscosities of their solutions. It was of interest to know whether similar relations would hold when one of the component solvents had a viscosity much greater than that of the other; in other words, whether the effect of one solvent on another follows the same laws, no matter what substances are used. The solvent eminently suited for this purpose is glycerol. Not only is its viscosity enormously greater than that of any other homogeneous liquid at ordinary temperatures, but several of its physical constants would lead us to expect glycerol to be well adapted as a solvent to making conductivity measurements. The dielectric constants and association factors of the solvents used in the previous work are given in table 103. The dielectric constants are taken from the work of Drude,<sup>1</sup> and were all determined in the neighborhood of 18°; and the association factors are taken from the work of Ramsay and Shields,<sup>2</sup> and refer to nearly the same temperature.

TABLE 103.

Solvent.	Dielectric constant.	Association factor.
Water.....	81.7	4.00
Methyl alcohol.....	32.5	3.43
Ethyl alcohol.....	21.7	2.74
Acetone.....	20.7	1.26

Glycerol has a dielectric constant of 16.5 at 18°, and hence, in terms of the Thomson-Nernst rule, should have a fairly high dissociating power. Moreover, if we assume Dutoit and Aston's hypothesis to hold even approximately for glycerol, the association factor of the latter, 1.80 at 20°, would lead to the same conclusion. The conductivity data will show that these expectations are well founded, and that glycerol is, in all probability, a solvent with a dissociating power rather above the average.

### GLYCEROL AS A SOLVENT.

It has, of course, been known for a long time that glycerol has remarkable solvent properties. Not only will it dissolve deliquescent salts, such as many compounds of lithium and calcium, but it also takes up large quantities of nearly all the halogen salts of the common metals, including even those that are difficultly soluble in water, as well as many sulphates, nitrates, etc. In addition, the alcohol groups of glycerol react with metallic oxides and hydroxides, forming glycerates by a process analogous to the solution of sodium or potassium hydroxides in alcohol.

<sup>1</sup>Weid. Ann., 60, 500.

<sup>2</sup>Zeit. phys. Chem., 12, 433 (1893).

In spite of the ease with which very pure glycerol can be obtained in large quantity, very little work has been done with solutions in it. In various branches of manufacture, and especially in pharmacy, it has long had extensive use as a solvent; but no systematic study has been made of the properties of its solutions.

Cattaneo<sup>1</sup> measured the conductivity of a number of halogen salts of the metals in glycerol, and found that the conductivities are smaller than the corresponding values in water or alcohol, but greater than those in ether. He also states that the molecular conductivity increases only in the case of chlorides. This last statement is not at all confirmed by the present work.

Schöttner<sup>2</sup> carried out an extensive investigation on the viscosity of glycerol and of some of its mixtures with water. Arrhenius<sup>3</sup> measured the viscosity of certain organic substances, including glycerol, in aqueous solution, and found that the decrease of  $\eta$  with rising temperature is greatest when  $\eta$  is large. Schall and van Rijn<sup>4</sup> determined the relative times of flow of various mixtures of glycerol with small quantities of water and alcohol.

#### CONDUCTIVITY APPARATUS.

The conductivity measurements were made by the Kohlrausch method, using a wire bridge and telephone receiver. The bridge wire was calibrated and found to be of uniform resistance throughout. The conductivity cells were of the form used by Jones and Bingham and subsequent workers in this laboratory. For use with the solutions in pure glycerol, two cells of a different type were used. The electrodes in one cell consisted of two concentric platinum cylinders, about 7 cm. long, and 18 and 22 mm. in diameter. They were maintained at a constant distance apart of about 2 mm. by means of several drops of fusion glass attached to the edges of the cylinders. The constant was very low, about 4.30. The other cell had as electrodes three cylinders, the outer and inner being joined by a thick branching platinum wire, and forming one electrode, while the middle cylinder formed the other. Drops of fusion glass also served here to keep the electrodes at a constant distance apart of about 1.5 mm. The cell constant was about 2.35. The electrodes of both cells were used without being covered with platinum black, and it was possible to obtain very sharp minima on the bridge with them. For instance, when the cell contained conductivity water, and a resistance of 1,000 or 2,000 ohms was introduced into the circuit, the bridge could easily be read at points 2 mm. on each side of the true minimum. This form of cell has proved itself to be especially adapted to work with very viscous solutions. The large electrode surface permits of the cylinders being several millimeters apart, without making the "capacity" of the cell too great; and this feature alone is of great advantage, as it allows very thick liquids to fill all the space between the electrodes, without the danger of imprisoning air bubbles. The escape of the latter is further facilitated by the vertical position of the cell walls. The "constants" of both cells showed only extremely slight variation throughout the work.

The conductivity measurements are expressed in reciprocal Siemens's units, and the cell constants were determined by means of a fiftieth-normal potassium chloride solution, the molecular conductivity of which was taken as 129.7 at 25°.

<sup>1</sup>Rend. Accad. Linc. [5], 2, II, 112 (1893).  
<sup>2</sup>Wien. Ber., 77, 2, 683 (1878).

<sup>3</sup>Zeit. phys. Chem., 1, 289 (1887).  
<sup>4</sup>Ibid., 23, 329 (1897).

Measurements were made at 25° and 35°. Glycerol, when maintained at 0° for a long period, undergoes a gradual change, resulting sometimes in the deposition of crystals. On this account, and for the reason that at low temperatures the substance is so extremely immobile that viscosity determinations are almost impossible, no measurements were made at 0°, as has been the custom in these investigations. The temperature coefficients of conductivity and viscosity are therefore not strictly comparable with those obtained by other workers for the same solutions between 0° and 25°.

The constant-temperature baths were of the form previously described, and were maintained constant to within 0.03° of the desired temperatures. The thermometers were compared with a certificated Reichsanstalt instrument. The measuring flasks were calibrated to hold aliquot parts of the true liter at 20°, and solutions were brought to within 0.2° of this temperature before filling to the mark.

#### SOLVENTS.

*Glycerol.*—The glycerol used was Kahlbaum's "Glycerin, 1.26." Two determinations of different lots gave the same density,  $D_{25}^{25} = 1.2586$ . The specific conductivity varied from  $0.5 \times 10^{-7}$  to  $0.7 \times 10^{-7}$  at 25°. Some of the glycerol was distilled under diminished pressure, boiling at 160° under a pressure of 6 mm. The specific conductivity was not changed by this process, and the remainder of the glycerol was used without further treatment.

*Water.*—The water was purified essentially by the method of Jones and Mackay,<sup>1</sup> with a slight modification. The practice heretofore has been to distil ordinary distilled water from acidified potassium dichromate to destroy organic matter and retain ammonia, and then to redistil from a weaker chromic acid solution, forcing the steam from the second distillation through a solution of barium hydroxide. There can be no doubt that water prepared in this way still contains large quantities of carbon dioxide. The extreme rapidity with which the current of steam passes through the alkaline solution makes it impossible for the latter to come in contact with all of the vapor, and some of the carbon dioxide escapes with the steam to be condensed, giving water with a conductivity which has generally been about  $2 \times 10^{-6}$  at 25°. If, however, the second distillation is made from a solution containing barium hydroxide instead of acidified dichromate, the conductivity of the water is lowered considerably. Nearly all of the carbon dioxide is retained, and the conductivity of the water thus purified has rarely risen over  $1.5 \times 10^{-6}$ , and was many times as low as 1.2. In addition, the alkaline solution, probably owing to the presence of the fine crystals of barium carbonate, boils more quietly than the acid solution, with entire absence of bumping.

*Ethyl and Methyl Alcohols.*—These were purified by boiling the commercial products with fresh lime for a day, and then distilling again from more lime without transferring the alcohol in the air. A third distillation from lime was made if the specific gravity of the second distillate showed the presence of any appreciable amount of water. Several more distillations were then made through a block-tin condenser. The conductivity of the ethyl alcohol ranged between  $1.2 \times 10^{-7}$  and  $1.8 \times 10^{-7}$ ,

<sup>1</sup>Amer. Chem. Journ., 17, 83 (1895).

although in one case it was as low as  $0.9 \times 10^{-7}$ . The value for the methyl alcohol was about  $1.5 \times 10^{-6}$  at  $25^{\circ}$ .

Work with mixtures containing acetone, which it was hoped would yield some interesting results, had to be given up, since glycerol and acetone are only slightly miscible.

The mixed solvents are made up on a volume basis, and in every case throughout the work, unless otherwise specified, "*n* per cent A and B" means *n* c.c. of solvent A diluted to 100 c.c. with solvent B.

#### SOLUTIONS.

All solutions were made on a volume-normal basis, at  $20^{\circ}$ , by direct weighing of the anhydrous salts. A tenth-normal mother-solution was first made, from which the fiftieth and hundredth normal solutions were prepared by dilution. The hundredth-normal solution then served as a mother-solution for the two-, four-, and eight-hundredth normal solutions, and from the last named the sixteen-hundredth normal was prepared. The dilutions were made by means of calibrated flasks and burettes. It was found that if a little time was given the solutions containing 25 and 50 per cent of glycerol would drain as completely as aqueous solutions, and the same calibration was used for all three. With the 75 per cent solutions, and especially with those in pure glycerol, the draining was incomplete, even though the burette stood two days. Accordingly, a different calibration was made for each of the three mixed solvents containing 75 per cent of glycerol, and for the pure glycerol itself. The amount to be delivered was run at a fixed rate of flow into a weighing-glass, and its weight divided by the density of the solvent at  $20^{\circ}$ . The difference between the volume thus found and the volume read off was the amount clinging to the walls of the burette, and this quantity, which was about 0.60 c.c. for 25 c.c. of glycerol, was added with each measurement of the solutions. It was of course necessary to run the solutions out between the same two points on the burette each time, as otherwise the mean hydrostatic pressure would vary, causing corresponding variations in the rate of flow, with a marked effect on the amount which did not drain out. This precaution is important, as shown by the fact that a volume of glycerol drawn off between 0 and 25 on the burette lacked 0.65 c.c. of 25 c.c., while the same apparent volume, taken between 24 and 49, was 0.35 c.c. less than the amount desired. The water calibration showed that this difference was not due to a great irregularity in the diameter of the burette. Another point that must be noted is the necessity of keeping the temperature of the working room constant while measuring glycerol. The changes in volume of the glycerol are inconsiderable compared with the great changes in fluidity, and a calibration made for  $20^{\circ}$  would, by reason of the much greater fluidity of glycerol at a higher temperature, be inaccurate at  $22^{\circ}$ .

In view of the fact that so little work has been done with solutions in glycerol, a few details of a practical nature may not be out of place. In spite of the great solvent power of glycerol, the actual rate of solution is very slow, and most substances can be dissolved only after a great deal of shaking and heating. It was customary in this work to heat the glycerol to almost  $100^{\circ}$  before adding it to the salt in the measuring flask. At this temperature glycerol is quite fluid, and its solvent action is greatly increased. Nevertheless, it required, with lithium bromide and cobalt

chloride, nearly three hours of practically continuous shaking, with the temperature at about 80° to 100°, to effect the complete solution of 1 or 2 grams of the salts in 100 c.c. of glycerol. Potassium iodide, on the other hand, dissolved as soon as the glycerol was warmed slightly, and gave a clear solution in less than five minutes. In view of the close relation of glycerol to the alcohols, and of the very slight solubility of potassium iodide in absolute alcohol, this behavior is surprising.

Much annoyance is caused by the ease with which glycerol imprisons air bubbles, which may require hours to rise. Especially is this likely to occur when the substance is poured into a burette. This difficulty may be obviated, however, by pouring the solutions in while hot, in which case the air bubbles will rise fairly rapidly; or by pouring the solutions in such a manner that the descending stream does not strike the walls of the burette except at the highest point to which the burette is to be filled. Thus manipulated, the glycerol flows down the burette walls without inclosing any air, and moreover, no time is lost in waiting for the upper part of the burette to drain before taking the initial reading.

#### VISCOSITY.

The determinations of viscosity were made by means of several Ostwald viscosimeters,<sup>1</sup> or this form as modified by Jones and Veazey.<sup>2</sup> For the solutions in pure glycerol, as well as for the solutions containing 75 per cent of glycerol, viscosimeters of very large bore were necessary. Two of these, made for us by Eimer and Amend, were very satisfactory. The small bulb had a capacity of about 4 c.c., and the larger of about 30 c.c. The "capillaries," having internal diameters of 1.1 and 2 mm., respectively, were 12 cm. long. As the time of flow of water through these viscosimeters was less than 10 seconds, it was of course necessary to calibrate them by using a more viscous liquid, the viscosity of which was known. For this purpose the viscosities of several solutions, containing about 50 per cent of glycerol, were determined in the smaller instruments, and then the times of flow of these liquids through the large viscosimeters were noted. A fixed amount of solution was introduced into the viscosimeter from a pipette, and after being raised to the upper mark by air pressure, was allowed to run through the capillary by its own weight. The times of flow were read with an accurate stop-watch. The viscosities were calculated from the formula

$$\frac{\eta}{\eta_0} = \frac{st}{s_0 t_0}$$

where  $\eta_0$ ,  $s_0$ , and  $t_0$  are the viscosity, density, and time of flow, respectively, of pure water, and  $\eta$ ,  $s$ , and  $t$  the corresponding values for the liquid in question. The values of  $\eta_0$  at 25° and 35° are taken from Thorpe and Rodger's work on viscosity, being 0.00891 at 25° and 0.00720 at 35°. Fluidity, expressed by  $\phi$ , is equal to  $\frac{1}{\eta}$ , and the temperature coefficients of fluidity are calculated from the formula

$$\text{temp. coef. } \phi = \frac{1}{\phi_{25}} \cdot \frac{\phi_{35} - \phi_{25}}{10}$$

The densities of the solutions were determined in pycnometers of the form described by Jones and Veazey.<sup>3</sup>

<sup>1</sup>Physiko-Chemische Messungen, 2d ed., p. 260.

<sup>2</sup>Phil. Trans., 185 A, 307 (1894).

<sup>3</sup>Zeit. phys. Chem., 61, 651 (1908).



The measurement of viscosity, for some reason, seems to be beset with much greater experimental error than would be expected, considering the simple nature of the operation. The values given in Landolt-Boernstein's "Tabellen" often show differences of more than 1 per cent in the results of various observers. During the present work it was found to be difficult to get results that would agree closely in duplicate determinations. It may at first sight be supposed that by taking three "steps" to determine the viscosities of the thicker solutions, as was done in this work, experimental error is introduced at each step, so that the values found by means of instruments with wide capillaries would necessarily be of doubtful accuracy. As a matter of fact, though experimental error is introduced, the departure of the values found from the true values is influenced much less by this fact than by an inherent difficulty in the method.

The Poisseuille formula for determining viscosity is  $v = \frac{\pi r^4 p t}{8 l \eta}$ , where  $v$  is the volume of liquid whose viscosity coefficient is  $\eta$ , which, under a pressure  $p$ , will flow in the time  $t$  through tube of length  $l$  and radius  $r$ . In deriving this formula, the liquid is considered as leaving the tube with a kinetic energy of zero, which, manifestly, is an impossible condition in practice. If the liquid flows out of the tube with a positive kinetic energy, a correction must be introduced. On rearranging the formula, with the correction it becomes

$$\eta = \frac{\pi r^4 p t}{8 v l} - \frac{v d}{8 \pi l}$$

where  $d$  is the density of the liquid. In determining viscosities by the relative method—that is, by means of the Ostwald viscosimeter—the corrected formula is rarely used. For two liquids flowing by their own weight through the same instrument, between the same differences in level,

$$\frac{\eta_1}{\eta_2} = \frac{p_1 t_1}{p_2 t_2}$$

But,

$$\frac{p_1}{p_2} = \frac{\rho_1 g h}{\rho_2 g h} = \frac{\rho_1}{\rho_2}$$

whence  $\frac{\eta_1}{\eta_2} = \frac{\rho_1 t_1}{\rho_2 t_2}$ , which is the ordinary formula.

It is evident from the corrected formula that when  $t$  is smallest the correction is greatest. Hence, a greater error is introduced by measuring the viscosity of a liquid whose time of flow is much greater than that of the standard than in the case of one with nearly the same viscosity as the standard. In other words, the error would be a minimum if  $t$  could be kept constant. Therefore, the error is kept lowest by using in each instrument liquids whose times of flow do not differ too greatly from  $t_0$ . As the correction is always negative, the viscosity of a liquid determined without using intermediate steps should be greater than if several viscosimeters are used. This is illustrated in the case of 75 per cent glycerol and methyl alcohol at 25°.  $T$  is the time of flow.

In table 104  $\eta$  is calculated by the following methods:

For viscosimeter A,  $\eta = \frac{0.00891 \times 4465 \times 1.1546}{1 \times 74.4} = 0.61735$ , 1.1546 being the density of 75 per cent glycerol and methyl alcohol.

TABLE 104.—Viscosity Determinations.

Viscosimeter.	T water.	T 50 per cent glycerol and methyl alcohol.	T 50 per cent glycerol and water.	T 75 per cent glycerol and methyl alcohol.	$\eta$
A	74.4	749.0	450.0	4465.0	0.61735
1	.....	74.7	45.7	445.6	0.6073
2	.....	.....	.....	141.7	0.6073

For viscosimeter 1, the viscosities of 50 per cent glycerol and water and 50 per cent glycerol and methyl alcohol were determined in A; then, from the times of flow of these solutions through 1, two values were obtained which were used to determine viscosities in 1, and the mean value of  $\eta$  for 75 per cent glycerol and methyl alcohol is determined from them, using  $T = 445.6$ . The same process is employed for viscosimeter 2. It is seen that  $\eta$  determined by direct comparison with water is greater, as it should be, than  $\eta$  determined by using liquids of intermediate viscosities in several instruments.

## LITHIUM BROMIDE.

The lithium bromide gave a flame test which showed no appreciable impurity. It was dried to constant weight at  $150^\circ$ , and was again dried after each exposure to the air. Table 105 gives the molecular conductivities of lithium bromide in pure glycerol at  $25^\circ$ ,  $35^\circ$ , and  $45^\circ$ . It will be noticed that while the values of  $\mu$ , are very small, yet they show a regular increase with dilution, as is the case with all liquids having a marked dissociating power.

TABLE 105.—Conductivity of Lithium Bromide in Glycerol at  $25^\circ$ ,  $35^\circ$ , and  $45^\circ$ .

V	$\mu$ , $25^\circ$	$\mu$ , $35^\circ$	$\mu$ , $45^\circ$	Temp. coefficients.	
				25 to $35^\circ$	35 to $45^\circ$
10	0.236	0.485	0.907	0.106	0.0871
50	0.260	0.540	1.010	0.107	0.0881
100	0.270	0.555	1.041	0.106	0.0875
200	0.272	0.565	1.050	0.106	0.0868
400	0.275	0.572	1.070	0.108	0.0871
800	0.280	0.579	1.085	0.107	0.0874
1,600	0.287	0.593	1.109	0.107	0.0871

Table 106 shows the conductivities of lithium bromide in various mixtures of glycerol with water, methyl alcohol, and ethyl alcohol. The results are plotted in figs. 60, 61, and 62. The curves show that the conductivities in the mixtures depart widely from the law of averages, there being a marked sagging of the curves in each case. The results are much like those obtained by Jones and Carroll with cadmium iodide in mixtures of water and methyl alcohol. No minimum is observed, nor, indeed, has any minimum appeared in all the work with glycerol solutions. This is not surprising. It is hardly probable that any mixture of glycerol with the less viscous solvents would have a viscosity greater than that of pure glycerol. It

FIG. 60.—Conductivity of Lithium Bromide in Glycerol-Water at 25°.

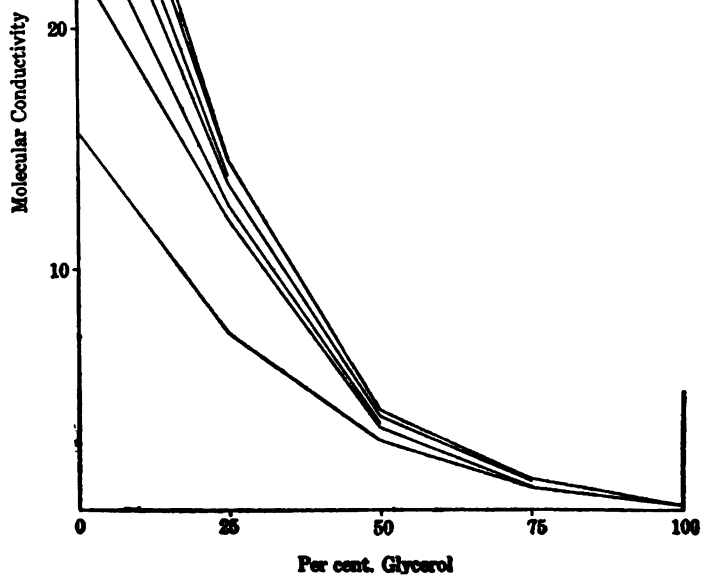
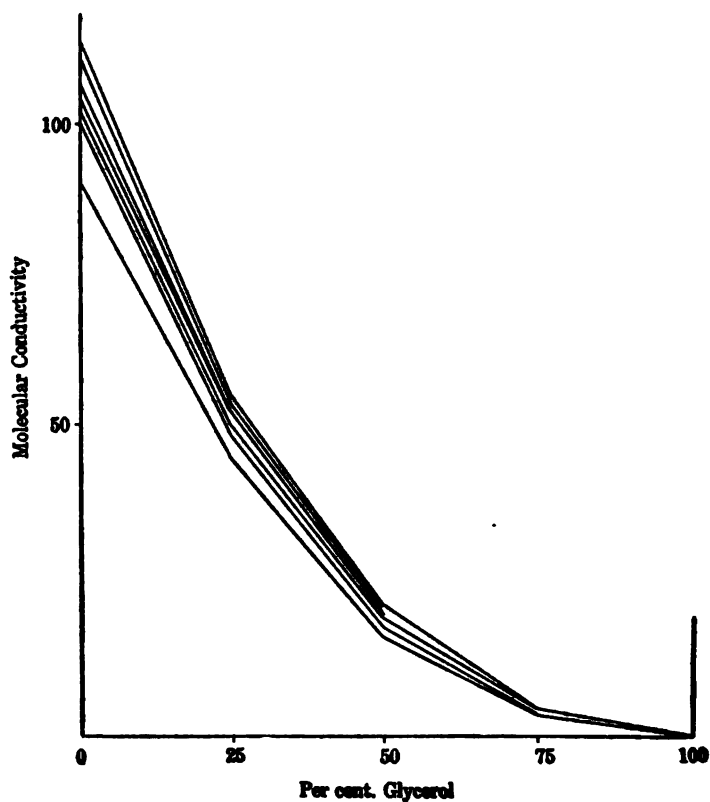


FIG. 61.—Conductivity of Lithium Bromide in Glycerol-Ethyl Alcohol at 25°.

is conceivable, however, that a mixture of glycerol with a very small percentage of water or alcohol might give a slight minimum in fluidity, but the difficulty of determining this point would be very great. At the same time, a similar minimum in the conductivity curves might make its appearance, and the parallelism of the two sets of curves, which is one of the points to be established, would not be changed, even if minima were found. At any rate, it is evident that in the case of mixtures of glycerol with the other three solvents used we have to deal with mixtures of the second class referred to above; that is, mixtures whose properties are not additive.

TABLE 106.—*Conductivities of Lithium Bromide in Various Solvents at 25° and 35°.*

V	Water.			Mixture of 25 per cent glycerol and water.			Mixture of 50 per cent glycerol and water.			Mixture of 75 per cent glycerol and water.		
	$\mu_{25^\circ}$	$\mu_{35^\circ}$	Temp. coef.	$\mu_{25^\circ}$	$\mu_{35^\circ}$	Temp. coef.	$\mu_{25^\circ}$	$\mu_{35^\circ}$	Temp. coef.	$\mu_{25^\circ}$	$\mu_{35^\circ}$	Temp. coef.
10	91.8	110.7	0.0205	45.6	57.4	0.0257	17.3	23.4	0.0351	3.84	5.96	0.0552
50	101.1	121.9	0.0206	49.6	62.5	0.0261	18.8	25.4	0.0348	4.23	6.56	0.0552
100	103.0	124.4	0.0208	50.8	64.0	0.0260	19.1	25.7	0.0346	4.27	6.63	0.0551
200	105.2	127.4	0.0219	52.8	66.7	0.0264	19.5	26.3	0.0350	4.43	6.89	0.0557
400	107.2	130.1	0.0213	52.2	65.5	0.0255	20.0	27.0	0.0351	4.51	6.99	0.0552
800	114.4	136.1	0.0222	54.0	69.4	0.0285	21.4	28.9	0.0352	4.40	6.89	0.0566
1,600	114.6	137.5	0.0200	54.9	71.5	0.0300	21.7	29.5	0.0361	4.47	6.99	0.0567
V	Ethyl alcohol.			Mixture of 25 per cent glycerol and ethyl alcohol.			Mixture of 50 per cent glycerol and ethyl alcohol.			Mixture of 75 per cent glycerol and ethyl alcohol.		
	$\mu_{25^\circ}$	$\mu_{35^\circ}$	Temp. coef.	$\mu_{25^\circ}$	$\mu_{35^\circ}$	Temp. coef.	$\mu_{25^\circ}$	$\mu_{35^\circ}$	Temp. coef.	$\mu_{25^\circ}$	$\mu_{35^\circ}$	Temp. coef.
10	15.8	18.4	0.0162	7.26	9.32	0.0283	2.91	4.25	0.0462	0.95	1.62	0.0710
50	23.0	26.7	0.0161	9.49	12.23	0.0289	3.40	4.97	0.0459	1.08	1.85	0.0711
100	25.9	30.3	0.0169	10.00	12.94	0.0294	3.61	5.29	0.0466	1.14	1.95	0.0719
200	29.2	33.6	0.0150	10.93	14.11	0.0291	3.85	5.61	0.0458	1.14	1.95	0.0718
400	31.1	36.5	0.0171	11.21	14.51	0.0294	3.85	5.64	0.0466	1.19	2.06	0.0720
800	33.3	39.2	0.0179	11.68	15.16	0.0298	3.98	5.86	0.0474	1.18	2.02	0.0713
1,600	35.1	41.6	0.0186	12.02	15.72	0.0308	4.02	5.89	0.0466	1.25	2.15	0.0724
V	Methyl alcohol.			Mixture of 25 per cent glycerol and methyl alcohol.			Mixture of 50 per cent glycerol and methyl alcohol.			Mixture of 75 per cent glycerol and methyl alcohol.		
	$\mu_{25^\circ}$	$\mu_{35^\circ}$	Temp. coef.	$\mu_{25^\circ}$	$\mu_{35^\circ}$	Temp. coef.	$\mu_{25^\circ}$	$\mu_{35^\circ}$	Temp. coef.	$\mu_{25^\circ}$	$\mu_{35^\circ}$	Temp. coef.
10	50.0	56.4	0.0127	21.3	25.8	0.0214	7.34	9.94	0.0350	1.73	2.78	0.0607
50	64.3	72.9	0.0134	25.5	30.9	0.0210	8.44	11.41	0.0353	2.01	3.21	0.0599
100	69.4	78.4	0.0129	27.1	32.9	0.0213	8.86	11.98	0.0352	2.13	3.38	0.0584
200	74.1	84.0	0.0134	28.9	35.3	0.0222	9.21	12.48	0.0355	2.30	3.38	0.0470
400	77.4	87.4	0.0129	29.2	35.7	0.0221	9.49	12.87	0.0356	.....	.....	.....
800	79.9	89.7	0.0124	30.3	36.8	0.0215	9.59	13.05	0.0361	2.20	3.55	0.0614
1,600	81.9	93.1	0.0137	31.2	38.3	0.0226	9.90	13.44	0.0357	2.17	3.49	0.0626

## COBALT CHLORIDE.

The cobalt chloride was first crystallized from conductivity water, to free it from traces of sulphates. The crystallization was continued until the mother-liquor no longer clouded a barium chloride solution. The salt was then partially dehydrated in a vacuum desiccator over sulphuric acid, after which it was pulverized and heated in the air until it had assumed a lavender color. After being again pulverized, it was placed in a hard-glass tube, and heated in a current of dry hydrochloric acid gas for several hours at 250°, during which it changed color to a pale pure blue.

The hydrochloric acid gas was then replaced by a stream of nitrogen dried over phosphorus pentoxide, and the tube allowed to cool slowly. The cobalt chloride gave a clear solution in water, which, however, when exposed to sunlight, deposited a very small quantity of a flocculent brown precipitate. Not enough of this could be obtained for a complete examination. It did not contain iron, and did not give the reactions of bivalent cobalt. It is thought to be a cobaltic compound, produced by some oxidizing action brought about by the sunlight. Solutions kept in the dark did not show this precipitate, even when allowed to stand over night; but ten minutes' exposure to bright sunlight was sufficient to cause the change. For this reason the conductivities of cobalt chloride in aqueous solution are considered a little uncertain, and are probably a little too high. Solutions in the alcohols and in glycerol were perfectly clear, and remained so indefinitely, sunlight having no effect on them.

The conductivities of cobalt chloride are given in tables 107 and 108. The conductivities in pure glycerol increase regularly, and are considerably higher than the corresponding values for lithium bromide. This is just what would be expected if glycerol is a normal dissociating solvent. Cobalt chloride would dissociate into three ions, while lithium bromide would give only two, and the conductivities of the former salt would accordingly be greater.

The results are plotted as curves in figs. 63, 64, and 65. The curves are in every respect analogous to those for lithium bromide, except in one minor point, to be seen in fig. 64. Here the values of conductivity of cobalt chloride in pure ethyl alcohol are abnormally

low (at least for all except the most dilute solutions), considering that it is a ternary electrolyte. Lithium bromide, for instance, in the tenth-normal solution in ethyl alcohol, has a molecular conductivity of 15.8 at 25°, and we should expect, other things

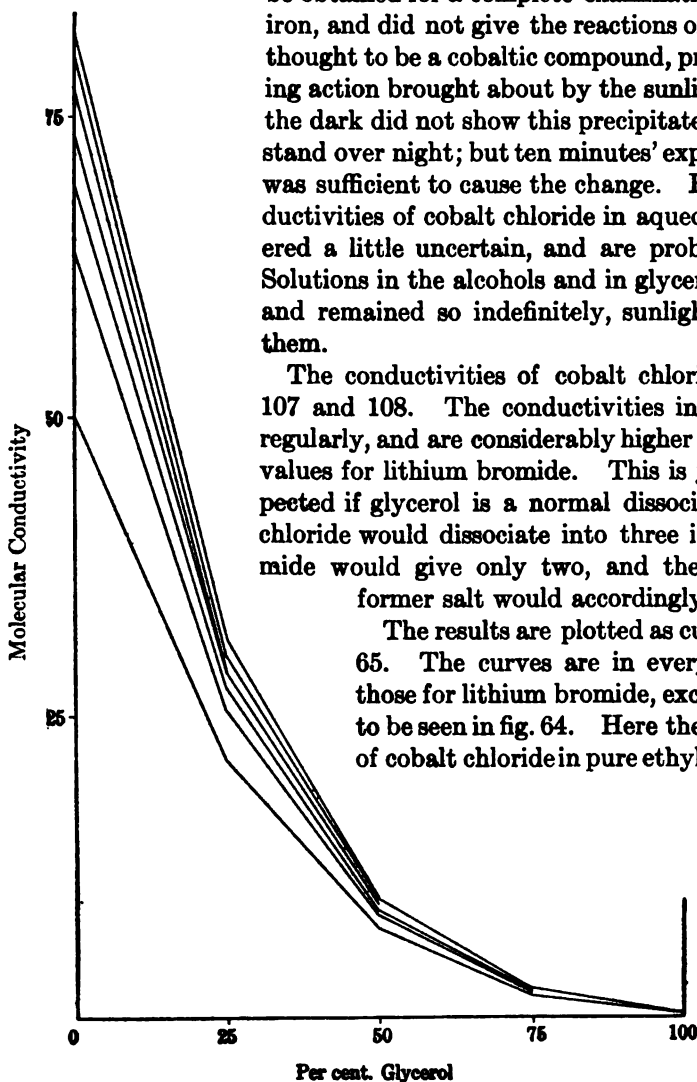
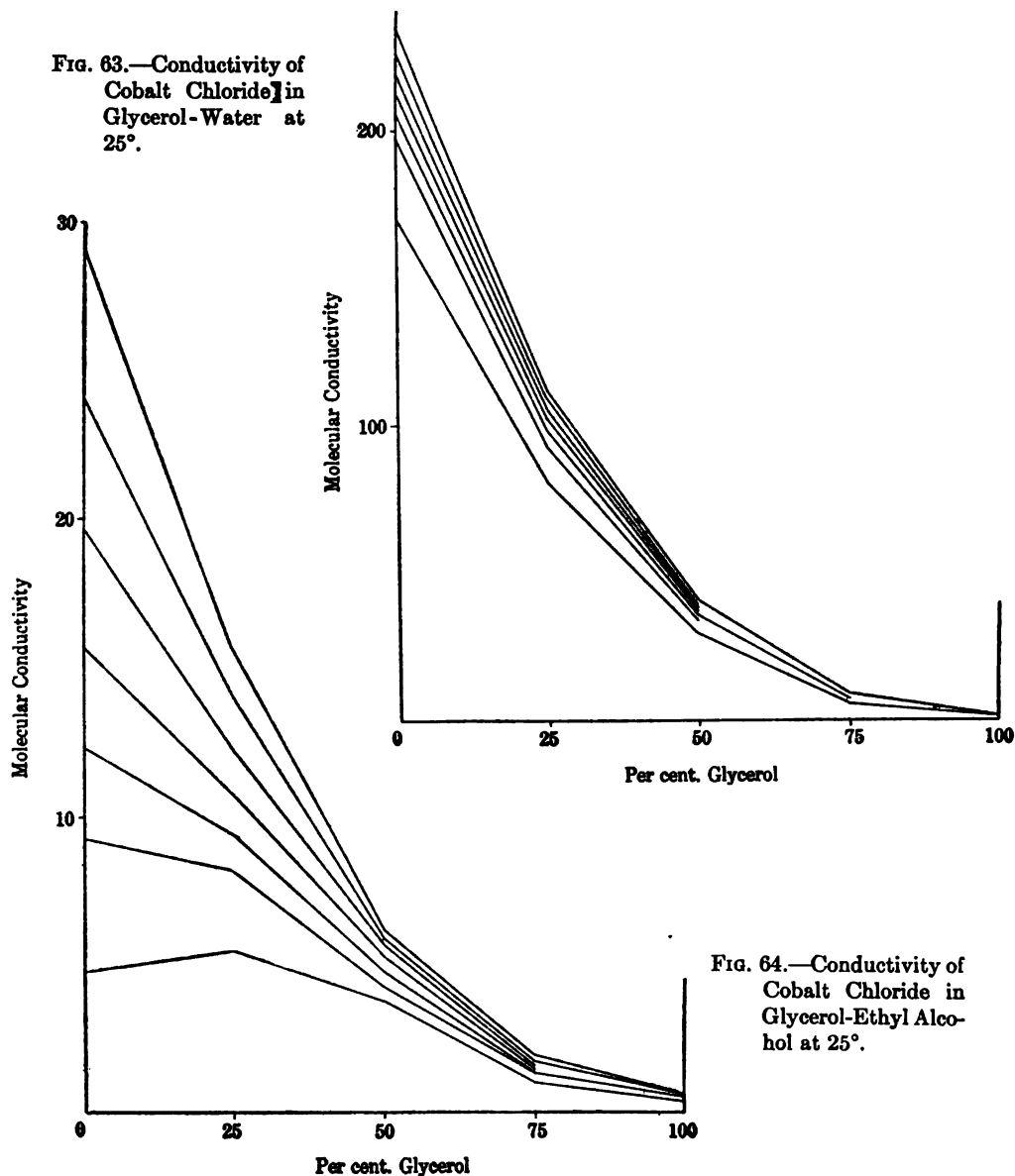


FIG. 62.—Conductivity of Lithium Bromide in Glycerol-Methyl Alcohol at 25°.

being equal, that cobalt chloride would give a value about 50 per cent greater than this. The value of  $\mu_{25^\circ}$  for cobalt chloride in ethyl alcohol is, however, only 4.71. But knowing that many of the halides of the heavy metals tend to form complexes when dissolved in organic solvents, it was suspected that these low results, at least in

the concentrated solutions, were due to partial polymerization of the cobalt chloride molecules. This point was tested by Mr. H. R. Kreider. He showed by the boiling-point method that the dissociation of cobalt chloride in ethyl alcohol, for concen-



trations ranging near tenth-normal, is apparently negative; or, in other words, the indicated molecular weight is greater than that calculated for  $\text{CoCl}_2$ . Some of his results are given here:

M.W. = 129.96.	Volume.....	8.1	13.0	13.3
	M. W. found....	155	134	131

The association appears in all three solutions, and since most other salts are dissociated 20 to 30 per cent in ethyl alcohol at these concentrations, we may consider the low conductivity of cobalt chloride in this case to be due to this cause. The same thing is shown in methyl alcohol solutions. The value of  $\mu$ , 25° for lithium bromide in tenth-normal solution is 50.0, against a corresponding value of 41.9 for cobalt chloride. The difference is not so striking here, probably because methyl alcohol is a stronger dissociant than ethyl alcohol.

TABLE 107.—*Conductivity of Cobalt Chloride in Glycerol at 25°, 35°, and 45°.*

V	$\mu$ , 25°	$\mu$ , 35°	$\mu$ , 45°	Temp. coefficients.	
				25 to 35°	35 to 45°
10	0.270	0.546	1.003	0.1023	0.0836
50	0.369	0.744	1.373	0.1015	0.0846
100	0.391	0.784	1.450	0.1004	0.0780
200	0.455	0.911	1.691	0.1004	0.0857
400	0.473	0.959	1.779	0.1027	0.0855
800	0.497	1.005	1.856	0.1011	0.0847
1,600	0.519	1.040	1.920	0.1002	0.0846

TABLE 108.—*Conductivities of Cobalt Chloride in Various Solvents at 25° and 35°.*

V	Water.			Mixture of 25 per cent glycerol and water.			Mixture of 50 per cent glycerol and water.			Mixture of 75 per cent glycerol and water.		
	$\mu$ , 25°	$\mu$ , 35°	Temp. coef.	$\mu$ , 25°	$\mu$ , 35°	Temp. coef.	$\mu$ , 25°	$\mu$ , 35°	Temp. coef.	$\mu$ , 25°	$\mu$ , 35°	Temp. coef.
10	168.9	204.7	0.0212	79.9	100.1	0.0252	28.8	38.7	0.0346	5.72	8.82	0.0542
50	195.5	236.8	0.0212	92.6	116.4	0.0258	33.7	45.4	0.0346	6.93	10.64	0.0536
100	204.2	246.7	0.0205	97.6	122.9	0.0259	35.4	47.6	0.0346	7.30	11.22	0.0536
200	212.6	256.5	0.0207	101.7	128.4	0.0262	37.1	49.7	0.0340	7.69	11.87	0.0543
400	219.4	267.9	0.0217	105.3	133.1	0.0264	38.1	51.2	0.0344	7.94	12.22	0.0540
800	226.6	276.9	0.0222	108.5	136.6	0.0260	39.4	53.3	0.0352	8.42	12.95	0.0538
1,600	232.6	282.6	0.0216	110.2	139.7	0.0267	40.4	54.5	0.0349	8.33	12.75	0.0531
V	Ethyl alcohol.			Mixture of 25 per cent glycerol and ethyl alcohol.			Mixture of 50 per cent glycerol and ethyl alcohol.			Mixture of 75 per cent glycerol and ethyl alcohol.		
	$\mu$ , 25°	$\mu$ , 35°	Temp. coef.	$\mu$ , 25°	$\mu$ , 35°	Temp. coef.	$\mu$ , 25°	$\mu$ , 35°	Temp. coef.	$\mu$ , 25°	$\mu$ , 35°	Temp. coef.
10	4.71	4.96	0.0053	5.43	6.70	0.0233	2.63	3.77	0.0436	0.95	1.58	0.0652
50	9.19	9.05	-0.0017	8.13	10.10	0.0243	3.65	5.11	0.0400	1.29	2.11	0.0638
100	12.18	11.92	-0.0021	9.30	11.52	0.0239	4.12	5.78	0.0402	1.41	2.32	0.0650
200	15.71	15.54	-0.0011	10.66	13.25	0.0243	4.66	6.53	0.0403	1.58	2.63	0.0662
400	19.56	19.64	0.0004	12.14	15.01	0.0236	5.14	7.32	0.0424	1.69	2.81	0.0666
800	24.07	24.91	0.0034	13.89	17.28	0.0244	5.65	8.03	0.0423	1.89	3.14	0.0660
1,600	28.78	30.38	0.0056	15.55	19.39	0.0246	5.86	8.46	0.0443	1.89	3.20	0.0662
V	Methyl alcohol.			Mixture of 25 per cent glycerol and methyl alcohol.			Mixture of 50 per cent glycerol and methyl alcohol.			Mixture of 75 per cent glycerol and methyl alcohol.		
	$\mu$ , 25°	$\mu$ , 35°	Temp. coef.	$\mu$ , 25°	$\mu$ , 35°	Temp. coef.	$\mu$ , 25°	$\mu$ , 35°	Temp. coef.	$\mu$ , 25°	$\mu$ , 35°	Temp. coef.
10	41.9	44.7	0.0066	19.6	23.0	0.0173	7.64	10.01	0.0310	1.90	3.00	0.0577
50	64.6	69.6	0.0077	27.8	32.6	0.0172	10.22	13.64	0.0334	2.55	3.99	0.0569
100	75.6	82.5	0.0098	32.1	37.7	0.0175	11.64	15.37	0.0323	2.81	4.43	0.0577
200	88.9	94.6	0.0065	36.6	43.1	0.0176	12.84	17.07	0.0330	3.12	4.35	0.0589
400	102.2	110.4	0.0080	40.7	48.2	0.0185	14.11	18.77	0.0330	3.55	5.36	0.0600
800	118.1	126.8	0.0078	44.8	53.4	0.0192	14.99	20.17	0.0346	3.51	5.63	0.0606
1,600	132.5	144.6	0.0092	48.8	57.4	0.0179	15.41	20.88	0.0355	3.59	5.76	0.0606

## POTASSIUM IODIDE.

Kahlbaum's pure potassium iodide was recrystallized, and dried to constant weight at 150°. It showed no appreciable impurity.

TABLE 109.—*Conductivity of Potassium Iodide in Glycerol at 25°, 35°, and 45°.*

V	$\mu_{25^\circ}$	$\mu_{35^\circ}$	$\mu_{45^\circ}$	Temp. coefficients,	
				25 to 35°	35 to 45°
10	0.291	0.607	1.189	0.1087	0.0844
50	0.326	0.667	1.275	0.1045	0.0912
100	0.324	0.670	1.257	0.1068	0.0875
200	0.334	0.687	1.284	0.1056	0.0870
400	0.338	0.686	1.282	0.1030	0.0871
800	0.346	0.708	1.325	0.1048	0.0871
1,600	0.352	0.717	1.326	0.1039	0.0849

TABLE 110.—*Conductivities of Potassium Iodide in Various Solvents at 25° and 35°.*

V	Water.			Mixture of 25 per cent glycerol and water.			Mixture of 50 per cent glycerol and water.			Mixture of 75 per cent glycerol and water.		
	$\mu_{25^\circ}$	$\mu_{35^\circ}$	Temp. coef.	$\mu_{25^\circ}$	$\mu_{35^\circ}$	Temp. coef.	$\mu_{25^\circ}$	$\mu_{35^\circ}$	Temp. coef.	$\mu_{25^\circ}$	$\mu_{35^\circ}$	Temp. coef.
10	125.6	150.4	0.0189	61.5	76.6	0.0244	23.9	30.8	0.0289	4.94	7.66	0.0552
50	131.6	156.5	0.0189	64.3	80.1	0.0246	24.4	32.3	0.0327	5.13	7.98	0.0555
100	133.6	159.3	0.0192	65.4	81.7	0.0249	24.6	32.8	0.0333	5.25	8.18	0.0559
200	135.8	162.1	0.0193	66.9	83.4	0.0249	24.9	33.2	0.0332	5.14	8.01	0.0559
400	137.2	163.7	0.0193	67.0	83.9	0.0251	25.1	33.4	0.0336	5.42	8.50	0.0569
800	138.9	165.9	0.0194	68.1	85.2	0.0252	25.4	34.1	0.0340	5.48	8.56	0.0563
1,600	140.0	167.5	0.0196	68.7	86.0	0.0252	25.5	34.5	0.0351	5.20	8.02	0.0545

V	Ethyl alcohol.			Mixture of 25 per cent glycerol and ethyl alcohol.			Mixture of 50 per cent glycerol and ethyl alcohol.			Mixture of 75 per cent glycerol and ethyl alcohol.		
	$\mu_{25^\circ}$	$\mu_{35^\circ}$	Temp. coef.	$\mu_{25^\circ}$	$\mu_{35^\circ}$	Temp. coef.	$\mu_{25^\circ}$	$\mu_{35^\circ}$	Temp. coef.	$\mu_{25^\circ}$	$\mu_{35^\circ}$	Temp. coef.
10	21.6	24.8	0.0146	9.50	12.27	0.0291	3.87	5.67	0.0466	1.19	2.05	0.0723
50	28.5	32.7	0.0148	11.35	14.68	0.0293	4.31	6.31	0.0466	1.19	2.11	0.0770
100	31.9	36.9	0.0156	12.12	15.79	0.0303	.....	.....	.....	1.33	2.28	0.0717
200	35.4	41.5	0.0171	12.88	16.87	0.0309	4.66	6.93	0.0484	1.39	2.37	0.0707
400	37.9	44.5	0.0173	13.40	17.56	0.0310	4.78	7.03	0.0470	1.42	2.43	0.0709
800	40.8	48.1	0.0177	13.99	18.33	0.0310	4.96	7.29	0.0471	1.46	2.51	0.0709
1,600	42.6	50.3	0.0179	14.62	18.70	0.0278	4.98	7.28	0.0460	1.49	2.50	0.0700

V	Methyl alcohol.			Mixture of 25 per cent glycerol and methyl alcohol.			Mixture of 50 per cent glycerol and methyl alcohol.			Mixture of 75 per cent glycerol and methyl alcohol.		
	$\mu_{25^\circ}$	$\mu_{35^\circ}$	Temp. coef.	$\mu_{25^\circ}$	$\mu_{35^\circ}$	Temp. coef.	$\mu_{25^\circ}$	$\mu_{35^\circ}$	Temp. coef.	$\mu_{25^\circ}$	$\mu_{35^\circ}$	Temp. coef.
10	65.5	72.9	0.0114	26.4	32.2	0.0219	9.1	12.5	0.0366	2.08	3.41	0.0635
50	79.6	89.1	0.0120	30.6	37.3	0.0220	10.2	13.9	0.0365	2.28	3.68	0.0619
100	84.0	94.1	0.0121	31.8	38.6	0.0218	10.4	14.2	0.0363	2.39	3.90	0.0635
200	90.9	102.1	0.0122	33.3	40.5	0.0217	10.8	14.8	0.0364	2.35	3.82	0.0624
400	94.8	106.6	0.0125	34.2	41.9	0.0224	11.1	15.1	0.0363	2.40	3.90	0.0631
800	98.0	111.2	0.0134	35.3	43.0	0.0218	11.5	15.6	0.0364	2.56	4.27	0.0663
1,600	100.8	113.4	0.0125	35.7	44.1	0.0233	11.8	16.1	0.0364	2.46	4.07	0.0648

Tables 109 and 110 give the conductivities of potassium iodide in glycerol and in the mixed solvents. Again, the conductivities increase nearly regularly with dilution, and are a little higher than those of lithium bromide, and about 50 per cent less



than the conductivities of cobalt chloride, as we should expect. The results in the mixtures are represented in figs. 66, 67, and 68, and are in every respect like those obtained for the other two salts. The conductivities are less than the average in each case.

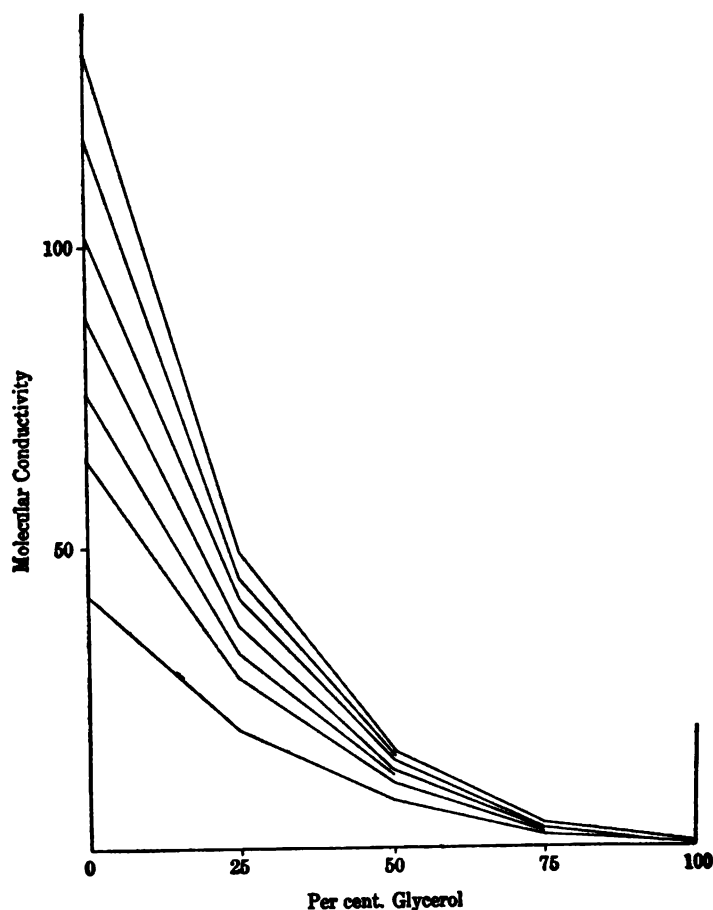


FIG. 65.—Conductivity of Cobalt Chloride in Glycerol-Methyl Alcohol at 25°.

#### TEMPERATURE COEFFICIENTS OF CONDUCTIVITY.

The most interesting features in this connection are the *very large temperature coefficients of conductivity of the solutions in pure glycerol*. In tenth-normal solution these are for lithium bromide, cobalt chloride, and potassium iodide, respectively, 10.6 per cent, 10.23 per cent, and 10.87 per cent between 25° and 35°, and 8.71 per cent, 8.36 per cent, and 8.44 per cent between 35° and 45°. *These are much the largest temperature coefficients of conductivity thus far observed between these temperatures, and they are closely related to the temperature coefficients of fluidity.*

FIG. 66.—Conductivity of Potassium Iodide in Glycerol-Water at 25°.

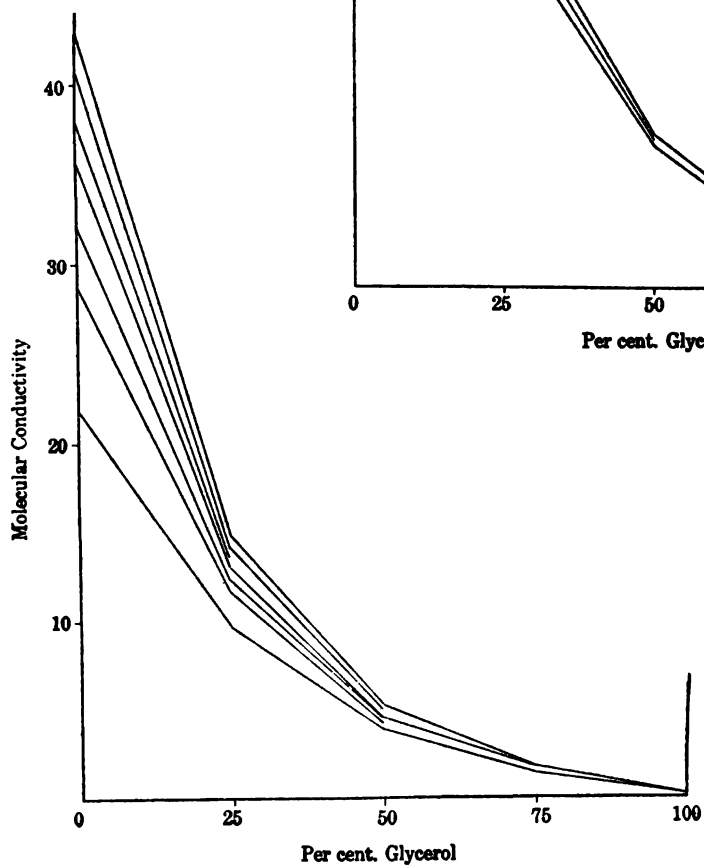
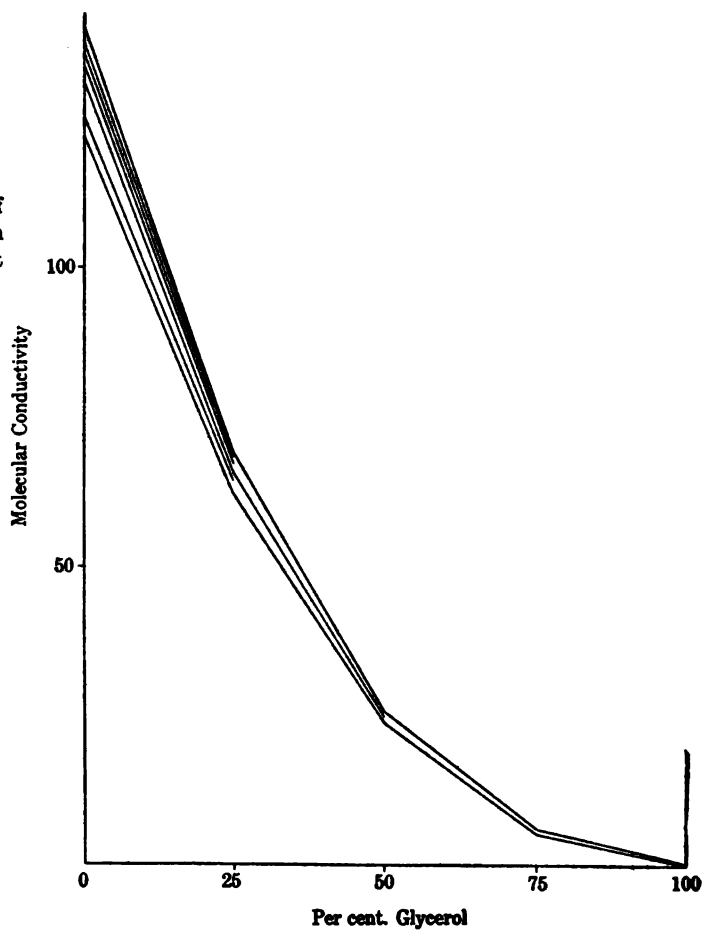


FIG. 67.—Conductivity of Potassium Iodide in Glycerol-Ethyl Alcohol at 25°.

In the solutions of cobalt chloride in ethyl alcohol, *negative temperature coefficients* of conductivity occur. These have also been noticed by Jones and McMaster in certain solutions of the same salt in mixtures of acetone and the alcohols. In the present case the temperature coefficient of the tenth-normal solution is positive, though very small, and in the fiftieth-normal solution it becomes negative. The temperature

coefficients reach a minimum in the hundredth-normal solution, and then increase regularly, again becoming positive in the dilute solutions. Temperature coefficients of conductivity in ethyl alcohol are always small, and it is known that the degree of ionization decreases with rising temperature. We have already proved that cobalt chloride in ethyl alcohol has a strong tendency to polymerize. The occurrence of negative temperature coefficients of conductivity, therefore, shows that the decrease in ionization due to rise in temperature, is more than sufficient to overcome the effect of increased ion velocity brought about by increased fluidity.

In the mixed solvents the temperature coefficients of conductivity in no case follow the law of averages, but, like the conductivities, are always less than the calculated values.

We have thus shown that for solutions in mixtures of glycerol with water or the alcohols, the molecular conductivities are always less than the averages calculated from the conductivities in the component solvents. Hence, we may conclude that glycerol is a solvent which, when mixed with another, gives a mixture whose properties are

not additive, and in this respect glycerol resembles water. In the three cases tested glycerol causes some change in the state of molecular aggregation of the other solvents, producing mixtures similar, in many ways, to mixtures of water with the alcohols or acetone. We can now

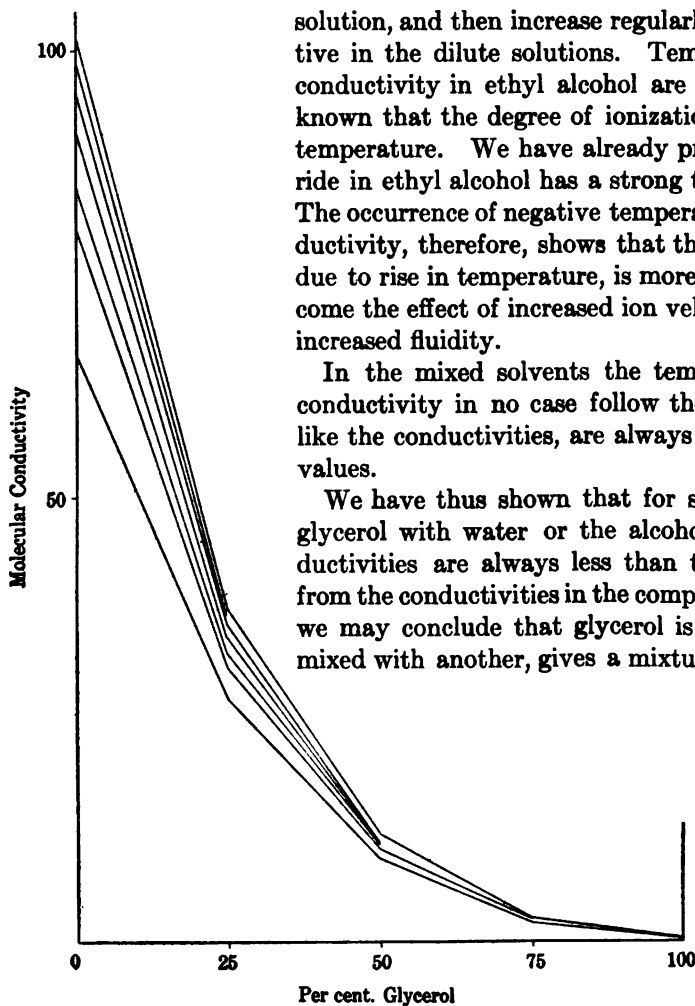


FIG. 68.—Conductivity of Potassium Iodide in Glycerol-Methyl Alcohol at 25°.

proceed to show that the departure from the law of averages is just as pronounced when we examine the fluidities of the mixtures of glycerol.

#### VISCOSITY AND FLUIDITY.

Tables 111 to 114, inclusive, give the viscosities and fluidities of the pure solvents, the mixed solvents, and the tenth-normal solutions of the three salts in these liquids.

The fluidities of the solutions are, as usual, in nearly every case less than those of the corresponding solvents. In three solutions, however, we have the phenomenon of negative viscosity. These are potassium iodide in water, and in 25 and 50 per cent glycerol and water, at both 25° and 35°. An explanation of negative viscosity has been given by Jones and Veazey.<sup>1</sup> It is interesting to find that the fluidity of even so immobile a liquid as 50 per cent glycerol and water is increased by the addition of potassium iodide. In the 75 per cent mixture the viscosity coefficient is again positive, but the difference between the viscosity of the mixture and of tenth-normal potassium iodide in it is not great. The salt does not lower the viscosity of pure glycerol, nor of any of the other solvents used.

TABLE 111.—*Viscosity and Fluidity of Solutions in Mixtures of Glycerol and Water at 25° and 35°.*

Solution.	Water.					25 per cent glycerol and water.				
	$\eta$ 25°	$\eta$ 35°	$\Phi$ 25°	$\Phi$ 35°	T. C. $\Phi$	$\eta$ 25°	$\eta$ 35°	$\Phi$ 25°	$\Phi$ 35°	T. C. $\Phi$
LiBr. ....	0.009011	0.00723	110.99	138.33	0.0246	0.02064	0.01552	48.45	64.44	0.0330
CoCl <sub>2</sub> ....	0.009209	0.00745	108.58	134.26	0.0237	0.02156	0.01624	46.49	61.65	0.0326
KI.....	0.008847	0.00719	113.02	139.06	0.0231	0.01991	0.01509	50.23	66.25	0.0319
Solvent..	0.00891	0.00720	112.25	138.89	0.0237	0.02003	0.01518	49.91	65.86	0.0319
	50 per cent glycerol and water.					75 per cent glycerol and water.				
	$\eta$ 25°	$\eta$ 35°	$\Phi$ 25°	$\Phi$ 35°	T. C. $\Phi$	$\eta$ 25°	$\eta$ 35°	$\Phi$ 25°	$\Phi$ 35°	T. C. $\Phi$
LiBr.....	0.06246	0.04346	16.01	23.01	0.0437	0.3330	0.2020	3.003	4.949	0.0647
CoCl <sub>2</sub> ....	0.06659	0.04632	15.02	21.59	0.0438	0.3645	0.2202	2.743	4.541	0.0656
I. K.....	0.06060	0.04252	16.50	23.52	0.0425	0.3246	0.1982	3.081	5.046	0.0638
Solvent..	0.06145	0.04272	16.27	23.41	0.0438	0.3203	0.1954	3.122	5.118	0.0639

TABLE 112.—*Viscosity and Fluidity of Solutions in Mixtures of Glycerol and Ethyl Alcohol at 25° and 35°.*

Solution.	Ethyl alcohol.					25 per cent glycerol and ethyl alcohol.				
	$\eta$ 25°	$\eta$ 35°	$\Phi$ 25°	$\Phi$ 35°	T. C. $\Phi$	$\eta$ 25°	$\eta$ 35°	$\Phi$ 25°	$\Phi$ 35°	T. C. $\Phi$
LiBr.....	0.01235	0.00864	80.92	101.37	0.0253	0.04574	0.03305	21.86	30.26	0.0384
CoCl <sub>2</sub> ....	0.01193	0.00828	83.80	101.75	0.0214	0.04919	0.03612	20.33	27.69	0.0362
KI.....	0.01177	0.00800	84.95	104.16	0.0266	0.04520	0.03290	22.12	30.39	0.0374
Solvent..	0.01110	0.00808	90.07	110.28	0.0224	0.04367	0.03188	22.90	31.37	0.0370
	50 per cent glycerol and ethyl alcohol.					75 per cent glycerol and ethyl alcohol.				
	$\eta$ 25°	$\eta$ 35°	$\Phi$ 25°	$\Phi$ 35°	T. C. $\Phi$	$\eta$ 25°	$\eta$ 35°	$\Phi$ 25°	$\Phi$ 35°	T. C. $\Phi$
LiBr.....	0.2275	0.1413	4.515	7.075	0.0588	1.1930	0.6455	0.8382	1.549	0.0848
CoCl <sub>2</sub> ....	0.2449	0.1569	4.084	6.375	0.0561	1.3530	0.7381	0.7391	1.355	0.0833
KI.....	0.2059	0.1327	4.856	7.537	0.0552	1.1005	0.6038	0.9089	1.656	0.0822
Solvent..	0.2053	0.1323	4.871	7.559	0.0552	1.0842	0.5971	0.9223	1.675	0.0816

But if we examine the viscosities of the solutions in pure glycerol, we see that the effect of the several salts on the viscosity of the solvent is in inverse ratio to the molecular volumes of the salts. Potassium iodide, with the largest molecular volume, increases the viscosity of glycerol less than does lithium bromide, which has a slightly smaller molecular volume. The latter salt, in turn, increases the viscosity of glycerol much less than does cobalt chloride, which has much the smallest molecular volume

<sup>1</sup>Amer. Chem. Jour., 37, 406 (1907).

of the three. *Relations exactly analogous to these* have been pointed out by Jones and Veazey, and the mechanism of the effect has been sufficiently discussed in the first part of this work.

The viscosity of pure glycerol at 25° (or 6.330) is 1,120 times that of methyl alcohol at the same temperature. A wide range of viscosity has thus been covered, yet the same relations hold that obtain in mixtures of the much more fluid solvents studied by Jones and his coworkers. The fluidities at 25° are plotted as curves in fig. 69. Curve I represents the fluidities of glycerol-methyl alcohol mixtures, curve II represents glycerol-water, and curve III represents glycerol-ethyl alcohol. The curves resemble the conductivity curves very closely, show the same sagging and have no minima.

TABLE 113.—*Viscosity and Fluidity of Solutions in Mixtures of Glycerol and Methyl Alcohol at 25° and 35°.*

Solution.	Methyl alcohol.					25 p. ct. glycerol and methyl alcohol.				
	$\eta$ 25°	$\eta$ 35°	$\Phi$ 25°	$\Phi$ 35°	T. C. $\Phi$	$\eta$ 25°	$\eta$ 35°	$\Phi$ 25°	$\Phi$ 35°	T. C. $\Phi$
LiBr.....	0.006097	0.005305	164.01	188.52	0.0149	0.02105	0.01647	47.51	60.72	0.0279
CoCl <sub>2</sub> ....	0.006365	0.005404	157.10	181.65	0.0135	0.02247	0.01735	44.51	57.64	0.0295
KI.....	0.006942	0.005149	168.31	194.21	0.0154	0.02019	0.01588	49.52	62.96	0.0272
Solvent..	0.005654	0.004918	176.86	204.59	0.0149	0.01962	0.01539	50.97	64.97	0.0274
	50 p. ct. glycerol and methyl alcohol.					75 p. ct. glycerol and methyl alcohol.				
	$\eta$ 25°	$\eta$ 35°	$\Phi$ 25°	$\Phi$ 35°	T. C. $\Phi$	$\eta$ 25°	$\eta$ 35°	$\Phi$ 25°	$\Phi$ 35°	T. C. $\Phi$
LiBr.....	0.1012	0.06945	9.882	14.40	0.0458	0.6525	0.3903	1.532	2.630	0.0717
CoCl <sub>2</sub> ....	0.1080	0.07451	9.258	13.42	0.0450	0.7379	0.4165	1.352	2.401	0.0776
KI.....	0.0936	0.06353	10.68	15.54	0.0474	0.6288	0.3637	1.590	2.750	0.0729
Solvent..	0.0928	0.06379	10.78	15.68	0.0454	0.6073	0.3532	1.647	2.815	0.0709

TABLE 114.—*Viscosity and Fluidity of Solutions in Glycerol at 25° and 35°.*

Solution.	$\eta$ 25°	$\eta$ 35°	$\Phi$ 25°	$\Phi$ 35°	T. C. $\Phi$
LiBr.....	6.786	3.192	0.1474	0.3133	0.1126
CoCl <sub>2</sub> .....	7.530	3.364	0.1328	0.2973	0.1261
KI.....	6.723	3.139	0.1487	0.3186	0.1143
Solvent.....	6.330	2.940	0.1580	0.3401	0.1153

The temperature coefficient of fluidity of pure glycerol between 25° and 35° is 11.53 per cent, and this is very nearly equal to the temperature coefficients of conductivity of the salts used in this work. In all the solutions the temperature coefficient of fluidity is greater than the temperature coefficients of conductivity, as has been hitherto observed in practically all cases. This is probably due partly to the decrease in dissociation with rising temperature.

It will be seen that in the majority of cases the temperature coefficient of fluidity of any solution is slightly greater than that of the solvent. As is known, dissociation decreases slightly with rising temperature. This would cause the solution at higher temperature to contain a greater number of whole molecules, whose volume would be equal to that of their component ions, but whose frictional surfaces would be less. This would decrease the total frictional surface of the particles in the solution and an increase in the fluidity would result, in addition to that caused by the ordinary

increase in the fluidity of the pure solvent. This relation does not hold for all of the temperature coefficients of fluidity, but the exceptions are not many, and it would seem that an explanation such as the above is at least partially correct.

A comparison of the conductivity and fluidity curves shows, then, that the two phenomena, in mixtures of glycerol with water or the alcohols, are very closely parallel. No minima are found, but every curve shows a falling below the straight line of averages. Hence, we must conclude that glycerol is a solvent resembling water more closely than it does the alcohols, in that mixtures containing it do not have additive properties. This resemblance to water comes out more strikingly when we examine the relative values of the conductivities of the three salts studied here, in the different pure solvents. In water, cobalt chloride, being a ternary electrolyte, has a greater conductivity than potassium iodide, and potassium iodide again has a conductivity greater than lithium bromide. The same order is found in glycerol. In ethyl alcohol, and in the tenth-normal solutions in methyl alcohol, the order is potassium iodide, lithium bromide, cobalt chloride. We have already shown that cobalt chloride in ethyl alcohol forms complexes. It is evident that in glycerol the same salt does not form complexes, but behaves like a normal ternary electrolyte in a strongly dissociating solvent. It seems to be broken down, at least partly, into three ions, even in the fairly concentrated solutions in glycerol; and in this point the latter resembles water rather than the alcohols.

The conductivities of the several electrolytes in pure glycerol do not reach limiting values in the dilutions here worked with, but the conductivities for dilutions of four-hundredth normal and greater are increasing very slowly; in other words, complete dissociation is probably reached in glycerol solutions at a comparatively small volume. This feature again recalls the dissociating action of water.

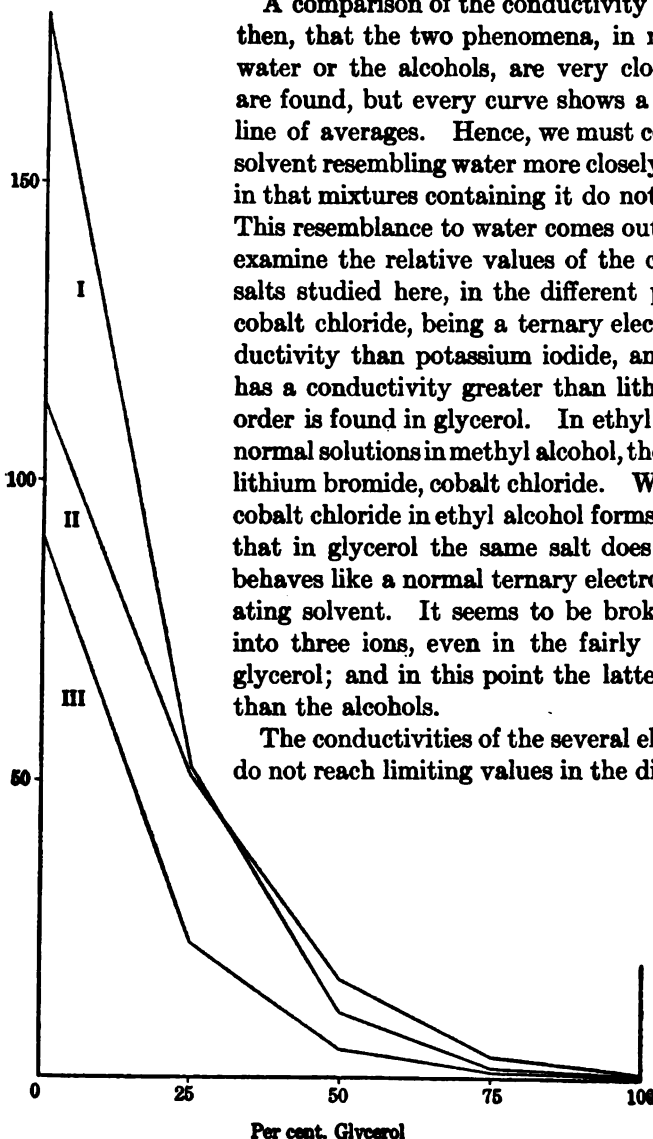


FIG. 69.—Fluidities of Glycerol Mixtures at 25°.

If we multiply 0.35, the highest conductivity obtained for potassium iodide in glycerol at 25°, by 6.330, the viscosity of the solvent at that temperature, the product is 2.22. Similarly, at 35° the product is 2.10. These numbers, nearly identical, represent lower limits, so to speak, of the product  $\mu_{\infty}\eta$  for glycerol. It will be recalled that Walden

found this value to be nearly a constant, independent of temperature, for about thirty organic solvents. Water and glycol, with values equal to 1.0 and 1.32 respectively, were exceptions. Glycerol thus becomes another exception with a product of at least 2.10. If we compare methyl alcohol, the simplest monacid carbinol, with glycol, the simplest diacid carbinol, and with glycerol, the simplest triacid carbinol, we see that conductivity does not increase proportional to fluidity, but to some fractional power of fluidity.

Solvent.....	CH <sub>3</sub> OH	C <sub>2</sub> H <sub>4</sub> (OH) <sub>2</sub>	C <sub>3</sub> H <sub>5</sub> (OH) <sub>3</sub>
$\mu_{\infty} \eta$ .....	0.72	1.32	2.10

A similar conclusion has been drawn by Green<sup>1</sup> from a study of the conductivity and viscosity of solutions of lithium chloride in water containing various amounts of sucrose, and he finds that  $\mu_{\infty} = K\phi^{0.7}$ .

#### SUMMARY OF FACTS ESTABLISHED.

(1) Glycerol, with water, or with methyl or ethyl alcohol, forms binary mixtures whose properties are not additive.

(2) The conductivity curves of three electrolytes in these mixtures in no case obey the law of averages.

(3) The same is true of the fluidity curves.

(4) The temperature coefficients of conductivity of solutions in pure glycerol are very large, and nearly identical with the temperature coefficients of fluidity.

(5) Glycerol, as a dissociating liquid, resembles water more closely than it does the alcohols.

(6) Conductivity increases with fluidity, but instead of increasing at the same rates, varies as some fractional power of fluidity.

<sup>1</sup>Journ. Chem. Soc., 93, 2049 (1908).

## WORK OF J. SAM GUY.

### EXPERIMENTAL.

#### APPARATUS.

In this investigation the Kohlrausch method of measuring conductivity has been employed, the improved Kohlrausch slide-wire bridge, resistance box, induction coil, and telephone receiver being used. The entire apparatus was made and carefully calibrated by Leeds, Northrup & Co., Philadelphia, and, in addition, the standard resistance was standardized by the United States Bureau of Standards, Washington, D. C. The new form of bridge is a great improvement over the ordinary Wheatstone bridge, both in convenience and accuracy. By means of such a bridge readings may be duplicated, under favorable conditions, to 0.1 mm.

The conductivity cells were of the same type as those described by Jones and Schmidt<sup>1</sup> and by Jones and Kreider.<sup>1</sup> Such cells, as has been stated, have very small constants, and hence are well adapted to measuring the conductivity of solutions with high resistances. In every case the cell constants were determined by means of a potassium chloride solution which was fiftieth normal, repeated determinations made at frequent intervals showing only slight variations in the cell constants throughout the entire investigation. The molecular conductivity of the fiftieth-normal potassium chloride solution was taken as 129.7 reciprocal Siemens units at 25°.

The constant-temperature baths were regulated by electrically controlled regulators, devised by Reid,<sup>2</sup> and were kept to within 0.02° of the desired temperature. The thermometers were carefully standardized against a certificated Reichsanstalt instrument. All flasks, burettes, and other apparatus were carefully calibrated, by weighing, to hold aliquot parts of the true liter at 20°.

#### SOLUTIONS.

For the work at 25°, 35°, and 45°, solutions were made up at 30°, while for the higher-temperature work the solutions were made up at 50°. In all cases the mother-solution was made by direct weighing of the carefully dried, anhydrous salt, and from this the N/50 and N/100 solutions were made by dilution. These solutions then served as the mother-solutions for the N/200 and N/400, from which, in turn, the N/800 and N/1600 solutions were made. The highest dilution was made by diluting the N/400 solution four times.

Measurements were not made at dilutions greater than 1,600, on account of the extremely high resistance and consequent difficulty in making the readings. In pure glycerol measurements were made at intervals of 5° from 25° to 75°, while in the mixed solvents they were made only at 25°, 35°, and 45°.

#### SOLVENTS.

*Glycerol.*—The glycerol used was Kahlbaum's best double-distilled product, and had a mean specific conductivity of about  $0.9 \times 10^{-7}$  at 25°. Schmidt had showed

<sup>1</sup>Amer. Chem. Journ., 45, 295 (1911).

<sup>2</sup>Ibid., 41, 148 (1909).



that redistillation did not essentially improve this glycerol. Its specific gravity showed that it contained about 0.02 per cent of water. The two lots obtained from Kahlbaum showed slightly different viscosities, as was indicated by the experimental results.

*Water.*—The water was purified by the method of Jones and Mackay,<sup>1</sup> with the modification as mentioned by Schmidt, and had a mean specific conductivity of  $1.5 \times 10^{-6}$  at 25°.

*Ethyl and Methyl Alcohols.*—The ethyl alcohol was purified by several distillations from the very best quality of lime, and block-tin condensers were always used. It had a mean conductivity of  $1.8 \times 10^{-7}$  at 25°. The methyl alcohol was first distilled from a small amount of dilute sulphuric acid and then several times from lime. It had a mean specific conductivity of  $2.0 \times 10^{-6}$  at 25°.

#### SALTS.

In all cases Kahlbaum's purest specimens were used, and these were recrystallized at least three times from conductivity water, carefully dried at 125°, and the solutions made by direct weighing.

#### VISCOSITY.

The viscosity measurements were made by means of the Ostwald viscosimeter as modified by Jones and Veazey,<sup>2</sup> and the size of the capillary so regulated as to be best adapted to glycerol measurements. The method of calibration has been discussed in detail by Schmidt. Viscosity was calculated from the formula;

$$\frac{\eta}{\eta_0} = \frac{St}{S_0 t_0}$$

in which  $\eta$  is the viscosity coefficient for the liquid in question,  $\eta_0$  that of water,  $S$  the specific gravity of the liquid,  $t$  the time of flow of the liquid,  $S_0$  the specific gravity of water at the given temperature, and  $t_0$  the time of flow of the water. Fluidity was calculated from the formula

$$\theta = \frac{1}{\eta}$$

where  $\theta$  represents the fluidity. The values of  $\eta_0$  are taken from the work of Thorpe and Rodger,<sup>3</sup> being 0.00891 at 25°, 0.00720 at 35°, 0.00598 at 45°, 0.005057 at 55°, 0.004355 at 65°, and 0.003786 at 75°.

#### TEMPERATURE COEFFICIENTS.

The temperature coefficients, both in per cent and in conductivity units, have been calculated, the latter being simply the actual increase in molecular conductivity per degree rise in temperature, while the former were calculated from the formula;

$$\text{Temp. coeff. of } \mu = \frac{1}{\mu_{25^\circ}} \frac{\mu_{35^\circ} - \mu_{25^\circ}}{10}$$

The temperature coefficients of fluidity were calculated in the same way.

Viscosity measurements were made only with the tenth-normal solutions, since at higher dilutions the difference between the viscosity of the solution and that of the solvent was very slight.

<sup>1</sup>Amer. Chem. Jour., 17, 83 (1895).

<sup>2</sup>Zeit. phys. Chem., 61, 641 (1906).

<sup>3</sup>Loc. cit.

TABLE 115.—*Molecular Conductivities (at 25°, 35°, and 45°) of Electrolytes in Pure Glycerol, together with Temperature Coefficients of Conductivity.*

Salt.	V	Molecular conductivity.			Temperature coefficients.			
					Per cent.		Conductivity units.	
		$\mu_v$ 25°	$\mu_v$ 35°	$\mu_v$ 45°	25 to 35°	35 to 45°	25 to 35°	35 to 45°
Potassium nitrate...	10	0.337	0.681	1.248	0.102	0.083	0.0344	0.0567
	50	0.368	0.754	1.384	0.105	0.083	0.0386	0.0630
	100	0.373	0.769	1.419	0.106	0.085	0.0396	0.0650
	200	0.397	0.818	1.509	0.106	0.084	0.0421	0.0691
	400	0.397	0.818	1.510	0.106	0.085	0.0421	0.0692
	800	0.412	0.845	1.569	0.105	0.086	0.0433	0.0724
Potassium chloride...	1,600	0.431	0.900	1.739	0.108	0.093	0.0469	0.0839
	10	0.385	0.772	1.413	0.100	0.083	0.0387	0.0641
	50	0.405	0.841	1.516	0.107	0.080	0.0436	0.0675
	100	0.412	0.844	1.538	0.105	0.082	0.0432	0.0694
	200	0.415	0.850	1.545	0.105	0.082	0.0435	0.0695
	400	0.439	0.852	1.571	0.094	0.084	0.0413	0.0719
Potassium bromide...	800	0.443	0.870	1.623	0.096	0.086	0.0427	0.0753
	1,600	0.536	0.915	1.630	0.071	0.078	0.0379	0.0715
	10	0.366	0.752	1.376	0.105	0.083	0.0386	0.0624
	50	0.369	0.752	1.396	0.104	0.086	0.0383	0.0644
	100	0.384	0.778	1.434	0.103	0.084	0.0394	0.0666
	200	0.385	0.782	1.435	0.103	0.083	0.0397	0.0653
Sodium chloride....	400	0.386	0.801	1.527	0.108	0.091	0.0415	0.0726
	800	0.390	0.821	1.578	0.110	0.092	0.0431	0.0757
	1,600	0.413	0.877	1.667	0.112	0.090	0.0464	0.0790
	10	0.328	0.666	1.223	0.103	0.084	0.0338	0.0557
	50	0.351	0.711	1.319	0.102	0.085	0.0360	0.0608
	100	0.353	0.720	1.350	0.104	0.087	0.0367	0.0630
Sodium iodide.....	200	0.372	0.753	1.409	0.102	0.087	0.0381	0.0666
	400	0.375	0.765	1.421	0.104	0.086	0.0390	0.0666
	800	0.391	0.806	1.588	0.106	0.097	0.0415	0.0732
	1,600	0.395	0.825	1.629	0.109	0.097	0.0430	0.0804
	10	0.342	0.690	1.265	0.105	0.083	0.0348	0.0575
	50	0.364	0.737	1.361	0.102	0.085	0.0373	0.0624
Sodium bromide....	100	0.366	0.745	1.372	0.103	0.084	0.0379	0.0627
	200	0.379	0.761	1.397	0.102	0.084	0.0382	0.0636
	400	0.397	0.786	1.452	0.098	0.085	0.0389	0.0666
	800	0.388	0.760	1.418	0.096	0.086	0.0372	0.0658
	1,600	0.447	0.840	1.557	0.088	0.085	0.0393	0.0717
	10	0.318	0.646	1.192	0.103	0.085	0.0328	0.0546
Sodium nitrate.....	50	0.331	0.678	1.260	0.105	0.086	0.0347	0.0582
	100	0.332	0.682	1.293	0.105	0.088	0.0350	0.0611
	200	0.359	0.734	1.367	0.104	0.087	0.0375	0.0633
	400	0.363	0.754	1.410	0.108	0.087	0.0391	0.0666
	800	0.379	0.784	1.465	0.107	0.087	0.0405	0.0681
	1,600	0.384	0.791	1.515	0.107	0.091	0.0407	0.0724
Sodium nitrate.....	10	0.303	0.617	1.129	0.103	0.083	0.0314	0.0512
	50	0.331	0.677	1.239	0.105	0.083	0.0346	0.0562
	100	0.338	0.707	1.284	0.110	0.082	0.0369	0.0577
	200	0.355	0.735	1.362	0.107	0.085	0.0380	0.0627
	400	0.358	0.737	1.378	0.106	0.087	0.0379	0.0641
	800	0.372	0.766	1.412	0.106	0.084	0.0394	0.0646
	1,600	0.386	0.796	1.544	0.106	0.094	0.0410	0.0748

TABLE 115.—*Molecular Conductivities (at 25°, 35°, and 45°) of Electrolytes in Pure Glycerol, together with Temperature Coefficients of Conductivity—Continued.*

Salt.	V	Molecular conductivity.			Temperature coefficients.			
					Per cent.		Conductivity units.	
		$\mu$ , 25°	$\mu$ , 35°	$\mu$ , 45°	25 to 35°	35 to 45°	25 to 35°	35 to 45°
Ammonium chloride.	10	0.393	0.801	1.452	0.104	0.081	0.0408	0.0651
	50	0.411	0.849	1.543	0.106	0.081	0.0438	0.0694
	100	0.426	0.879	1.605	0.106	0.083	0.0453	0.0726
	200	0.427	0.889	1.623	0.108	0.082	0.0462	0.0734
	400	0.432	0.889	1.639	0.106	0.084	0.0457	0.0750
	800	0.440	0.931	1.696	0.111	0.082	0.0491	0.0765
	1,600	0.442	0.948	1.709	0.112	0.080	0.0506	0.0761
Ammonium bromide.	10	0.373	0.758	1.391	0.103	0.083	0.0385	0.0633
	50	0.391	0.802	1.490	0.105	0.085	0.0411	0.0688
	100	0.397	0.824	1.531	0.107	0.086	0.0427	0.0707
	200	0.422	0.878	1.632	0.107	0.086	0.0456	0.0754
	400	0.430	0.889	1.642	0.107	0.085	0.0459	0.0753
	800	0.444	0.926	1.694	0.109	0.083	0.0482	0.0768
	1,600	0.492	1.034	1.864	0.110	0.080	0.0542	0.0830
Ammonium nitrate.	10	0.345	0.696	1.272	0.102	0.083	0.0351	0.0576
	50	0.379	0.778	1.440	0.105	0.085	0.0399	0.0662
	100	0.392	0.805	1.488	0.106	0.085	0.0413	0.0683
	200	0.407	0.840	1.547	0.106	0.084	0.0433	0.0707
	400	0.417	0.869	1.594	0.108	0.083	0.0452	0.0725
	800	0.396	0.825	1.579	0.108	0.091	0.0429	0.0754
	1,600	0.437	0.917	1.651	0.109	0.080	0.0480	0.0734
Barium chloride....	10	0.315	0.664	1.221	0.111	0.084	0.0349	0.0557
	50	0.432	0.915	1.695	0.111	0.085	0.0483	0.0780
	100	0.464	0.978	1.803	0.111	0.084	0.0514	0.0825
	200	0.502	1.056	1.951	0.110	0.085	0.0554	0.0895
	400	0.520	1.101	1.994	0.112	0.081	0.0581	0.0893
	800	0.561	1.197	2.230	0.113	0.086	0.0636	0.1033
	1,600	0.565	1.332	2.368	0.136	0.078	0.0767	0.1036
Barium bromide....	10	0.330	0.696	1.314	0.111	0.089	0.0366	0.0618
	50	0.396	0.832	1.566	0.110	0.088	0.0436	0.0734
	100	0.426	0.900	1.698	0.111	0.089	0.0474	0.0798
	200	0.443	0.938	1.774	0.112	0.089	0.0495	0.0836
	400	0.474	1.001	1.896	0.111	0.089	0.0527	0.0895
	800	0.520	1.127	2.115	0.116	0.088	0.0607	0.0988
	1,600	0.530	1.157	2.200	0.118	0.090	0.0627	0.1043
Barium nitrate.....	10	0.246	0.517	0.959	0.110	0.085	0.0271	0.0442
	50	0.347	0.738	1.367	0.113	0.085	0.0391	0.0629
	100	0.368	0.792	1.479	0.115	0.087	0.0424	0.0687
	200	0.401	0.871	1.634	0.117	0.088	0.0470	0.0763
	400	0.414	0.904	1.719	0.117	0.090	0.0490	0.0815
	800	0.456	0.988	1.871	0.117	0.090	0.0532	0.0883
	1,600	0.462	0.991	1.897	0.114	0.091	0.0529	0.0906
Calcium bromide....	10	0.245	0.519	0.972	0.112	0.087	0.0274	0.0453
	50	0.324	0.687	1.298	0.112	0.089	0.0363	0.0611
	100	0.340	0.729	1.374	0.114	0.088	0.0389	0.0645
	200	0.373	0.803	1.514	0.115	0.089	0.0430	0.0711
	400	0.386	0.833	1.556	0.116	0.090	0.0447	0.0723
	800	0.395	0.882	1.721	0.123	0.095	0.0487	0.0839
	1,600	0.408	0.909	1.743	0.123	0.092	0.0501	0.0834

TABLE 115.—*Molecular Conductivities (at 25°, 35°, and 45°) of Electrolytes in Pure Glycerol, together with Temperature Coefficients of Conductivity—Continued.*

Salt.	V	Molecular conductivity.			Temperature coefficients.			
					Per cent.		Conductivity units.	
		$\mu$ , 25°	$\mu$ , 35°	$\mu$ , 45°	25 to 35°	35 to 45°	25 to 35°	35 to 45°
Strontium bromide...	10	0.264	0.556	1.054	0.111	0.089	0.0292	0.0498
	50	0.340	0.717	1.362	0.112	0.090	0.0377	0.0645
	100	0.365	0.776	1.468	0.112	0.089	0.0411	0.0692
	200	0.388	0.831	1.581	0.113	0.090	0.0443	0.0750
	400	0.391	0.876	1.659	0.119	0.089	0.0485	0.0783
	800	0.409	0.886	1.681	0.117	0.089	0.0477	0.0795
	1,600	0.428	0.924	1.758	0.117	0.090	0.0496	0.0834
Strontium nitrate...	10	0.235	0.501	0.934	0.113	0.086	0.0266	0.0433
	50	0.323	0.687	1.292	0.112	0.088	0.0364	0.0605
	100	0.349	0.744	1.394	0.113	0.087	0.0395	0.0650
	200	0.392	0.833	1.563	0.112	0.088	0.0441	0.0730
	400	0.401	0.872	1.686	0.117	0.093	0.0471	0.0814
	800	0.411	0.891	1.671	0.117	0.087	0.0480	0.0780
	1,600	0.449	0.945	1.759	0.110	0.086	0.0496	0.0814
Cobalt chloride.....	10	0.270	0.546	1.003	0.102	0.084	0.0276	0.0457
	50	0.369	0.744	1.373	0.101	0.085	0.0375	0.0629
	100	0.391	0.784	1.450	0.100	0.085	0.0393	0.0666
	200	0.455	0.911	1.691	0.100	0.086	0.0456	0.0780
	400	0.473	0.959	1.779	0.108	0.085	0.0486	0.0820
	800	0.497	1.005	1.856	0.102	0.085	0.0508	0.0851
	1,600	0.519	1.040	1.920	0.100	0.085	0.0521	0.0880
Cobalt bromide.....	10	0.364	0.744	1.370	0.104	0.084	0.0380	0.0626
	50	0.460	0.932	1.702	0.103	0.083	0.0472	0.0770
	100	0.468	0.953	1.743	0.104	0.083	0.0485	0.0790
	200	0.514	1.045	1.911	0.103	0.083	0.0531	0.0866
	400	0.533	1.076	1.967	0.102	0.083	0.0543	0.0891
	800	0.552	1.103	2.031	0.100	0.084	0.0551	0.0928
	1,600	0.564	1.091	2.005	0.093	0.084	0.0527	0.0914

TABLE 116.—*Molecular Conductivities (at 55°, 65°, and 75°) of Electrolytes in Glycerol, together with Temperature Coefficients of Conductivity.*

Salt.	V	Molecular conductivity.			Temperature coefficients.			
					Per cent.		Conductivity units.	
		$\mu$ , 55°	$\mu$ , 65°	$\mu$ , 75°	55 to 65°	65 to 75°	55 to 65°	65 to 75°
Potassium chloride..	10	2.391	3.755	5.601	0.057	0.049	0.1364	0.1846
	50	2.601	4.124	6.176	0.059	0.050	0.1523	0.2052
	100	2.707	4.252	6.300	0.057	0.048	0.1545	0.2048
	200	2.734	4.341	6.489	0.059	0.050	0.1607	0.2148
	400	2.738	4.470	6.691	0.063	0.050	0.1732	0.2221
	800	2.817	4.562	6.862	0.062	0.050	0.1745	0.2300
	1,600	2.940	4.693	6.891	0.060	0.047	0.1753	0.2198
Potassium bromide..	10	2.293	3.619	5.332	0.058	0.047	0.1326	0.1713
	50	2.453	3.906	4.786	0.059	0.048	0.1453	0.1880
	100	2.557	4.062	6.080	0.059	0.050	0.1505	0.2018
	200	2.606	4.122	6.154	0.057	0.049	0.1516	0.2032
	400	2.680	4.275	6.317	0.059	0.048	0.1595	0.2042
	800	2.705	4.286	6.408	0.058	0.050	0.1581	0.2122
	1,600	2.770	4.400	6.897	0.059	0.057	0.1630	0.2497

TABLE 116.—*Molecular Conductivities (at 55°, 65°, and 75°) of Electrolytes in Glycerol, together with Temperature Coefficients of Conductivity—Continued.*

Salt.	V	Molecular conductivity.			Temperature coefficients.			
					Per cent.		Conductivity units.	
		$\mu$ , 55°	$\mu$ , 65°	$\mu$ , 75°	55 to 65°	65 to 75°	55 to 65°	65 to 75°
Sodium bromide....	10	2.006	3.153	4.763	0.057	0.051	0.1147	0.1610
	50	2.203	3.500	5.262	0.059	0.050	0.1297	0.1762
	100	2.299	3.656	5.504	0.059	0.050	0.1357	0.1848
	200	2.325	3.683	5.566	0.058	0.051	0.1358	0.1883
	400	2.397	3.715	5.753	0.055	0.056	0.1318	0.2038
	800	2.438	3.760	5.864	0.054	0.055	0.1322	0.2104
Sodium iodide.....	1,600	2.493	3.965	5.938	0.059	0.050	0.1472	0.1973
	10	2.101	3.300	4.878	0.057	0.048	0.1199	0.1578
	50	2.246	3.568	5.407	0.059	0.051	0.1322	0.1839
	100	2.347	3.731	5.590	0.059	0.050	0.1384	0.1859
	200	2.377	3.756	5.604	0.058	0.049	0.1379	0.1848
	400	2.441	3.865	5.822	0.058	0.051	0.1424	0.1957
Ammonium chloride..	800	2.410	3.833	5.745	0.059	0.050	0.1423	0.1912
	1,600	2.591	4.263	6.415	0.064	0.064	0.1672	0.2152
	10	2.785	4.313	6.285	0.054	0.046	0.1528	0.1972
	50	2.863	4.498	6.593	0.057	0.047	0.1635	0.2095
	100	3.109	4.821	7.033	0.055	0.046	0.1712	0.2212
	200	3.144	4.789	7.018	0.052	0.046	0.1645	0.2229
Ammonium nitrate..	400	3.146	4.858	7.162	0.054	0.046	0.1712	0.2304
	800	3.252	5.051	7.409	0.055	0.047	0.1799	0.2358
	1,600	3.224	5.015	7.351	0.056	0.046	0.1791	0.2336
	10	2.558	3.942	5.873	0.054	0.049	0.1384	0.1931
	50	2.766	4.250	6.310	0.054	0.048	0.1484	0.2060
	100	2.907	4.458	6.772	0.053	0.052	0.1551	0.2314
Barium nitrate.....	200	2.947	4.580	6.844	0.055	0.049	0.1633	0.2264
	400	3.015	4.661	6.956	0.054	0.049	0.1646	0.2295
	800	3.103	4.754	7.107	0.053	0.049	0.1651	0.2353
	1,600	3.194	4.923	8.372	0.054	0.050	0.1729	0.2449
	10	2.262	3.565	5.300	0.058	0.049	0.1303	0.1735
	50	2.856	4.480	6.725	0.057	0.050	0.1624	0.2245
Strontium chloride..	100	3.106	4.906	7.304	0.058	0.049	0.1800	0.2394
	200	3.362	5.269	7.858	0.057	0.049	0.1907	0.2589
	400	3.555	5.629	8.555	0.058	0.052	0.2074	0.2926
	800	3.757	5.987	9.046	0.060	0.051	0.2230	0.3059
	1,600	3.942	6.236	9.466	0.058	0.052	0.2294	0.3230
	10	2.243	3.576	5.378	0.059	0.050	0.1333	0.1802
Cobalt chloride.....	50	2.727	4.312	6.442	0.058	0.049	0.1585	0.2130
	100	2.900	4.610	6.880	0.059	0.049	0.1710	0.2270
	200	3.101	4.946	7.423	0.059	0.050	0.1845	0.2477
	400	3.314	5.257	7.855	0.059	0.049	0.1943	0.2598
	800	3.389	5.400	8.078	0.059	0.049	0.2011	0.2678
	1,600	3.645	5.750	8.780	0.058	0.053	0.2105	0.3030
Cobalt bromide.....	10	1.789	2.778	4.102	0.055	0.048	0.0989	0.1324
	50	2.373	3.686	5.447	0.055	0.048	0.1313	0.1761
	100	2.610	4.074	6.024	0.056	0.048	0.1464	0.1950
	200	2.890	4.513	6.687	0.056	0.048	0.1623	0.2174
	400	3.104	4.864	7.236	0.057	0.049	0.1760	0.2372
	800	3.286	5.178	7.750	0.057	0.050	0.1892	0.2572
Cobalt bromide.....	1,600	3.471	5.503	8.247	0.058	0.050	0.2032	0.2744
	10	2.340	3.676	5.462	0.057	0.048	0.1336	0.1786
	50	2.905	4.561	6.841	0.057	0.050	0.1656	0.2280
	100	2.952	4.628	6.954	0.057	0.050	0.1676	0.2326
	200	3.229	5.068	7.584	0.057	0.050	0.1839	0.2516
	400	3.338	5.242	7.904	0.057	0.051	0.1904	0.2662
Cobalt bromide.....	800	3.429	5.420	8.549	0.058	0.060	0.1991	0.3129
	1,600	3.400	5.399	8.112	0.059	0.051	0.1999	0.2713

TABLE 117.—Data for the Molecular Conductivity and Temperature Coefficients of Conductivity (at 25°, 35°, and 45°), in Per Cent and in Conductivity Units, for Potassium Chloride, Sodium Nitrate, Ammonium Bromide, and Strontium Chloride in the Various Mixtures of Glycerol with Water, Methyl Alcohol, and Ethyl Alcohol.

Salt.	V	Molecular conductivity.			Temperature coefficients.			
					Per cent.		Conductivity units.	
		$\mu_0$ 25°	$\mu_0$ 35°	$\mu_0$ 45°	25 to 35°	35 to 45°	25 to 35°	35 to 45°
Potassium chloride in a mixture of 75 per cent glycerol with water.....	10	5.33	8.29	11.92	0.055	0.044	0.296	0.363
	50	5.78	9.00	13.04	0.056	0.045	0.322	0.404
	100	5.86	9.08	13.09	0.055	0.044	0.322	0.401
	200	6.07	9.39	13.71	0.055	0.046	0.332	0.432
	400	6.38	9.89	14.47	0.055	0.046	0.351	0.458
	800	6.61	10.27	14.66	0.055	0.043	0.366	0.439
	1,600	6.51	10.15	14.92	0.056	0.047	0.364	0.477
Potassium chloride in a mixture of 50 per cent glycerol with water.....	10	23.55	31.59	40.28	0.034	0.027	0.804	0.869
	50	25.17	33.89	43.84	0.034	0.029	0.872	0.995
	100	26.00	34.73	45.68	0.034	0.032	0.873	1.095
	200	26.30	35.17	45.73	0.034	0.030	0.887	1.056
	400	28.52	38.35	49.63	0.034	0.029	0.983	1.128
	800	29.21	39.28	50.37	0.034	0.028	1.007	1.109
	1,600	30.57	41.12	52.33	0.034	0.027	1.055	1.121
Potassium chloride in a mixture of 25 per cent glycerol with water.....	10	59.81	74.52	90.16	0.025	0.021	1.471	1.564
	50	65.00	81.89	98.63	0.026	0.020	1.689	1.674
	100	66.68	82.94	101.08	0.024	0.022	1.626	1.814
	200	68.13	85.34	103.36	0.025	0.021	1.721	1.802
	400	74.87	93.04	112.24	0.024	0.021	1.817	1.920
	800	77.85	96.30	116.68	0.024	0.021	1.845	2.038
	1,600	78.99	98.98	121.32	0.025	0.023	1.999	2.234
Potassium chloride in water .....	10	120.4	143.0	166.7	0.019	0.016	2.26	2.37
	50	129.7	154.5	181.2	0.019	0.017	2.48	2.67
	100	132.0	158.5	184.7	0.020	0.017	2.65	2.62
	200	135.3	161.6	189.3	0.019	0.017	2.63	2.77
	400	137.7	165.4	193.8	0.020	0.017	2.77	2.84
	800	138.1	165.8	194.8	0.020	0.017	2.77	2.90
	1,600	140.3	169.3	197.9	0.021	0.017	2.90	2.86
Potassium chloride in a mixture of 75 per cent glycerol with ethyl alcohol.....	10	1.21	2.05	3.26	0.069	0.059	0.084	0.121
	50	1.31	2.25	3.59	0.072	0.060	0.094	0.134
	100	1.35	2.34	3.69	0.073	0.058	0.099	0.135
	200	1.41	2.43	3.90	0.072	0.060	0.102	0.147
	400	1.53	2.63	4.22	0.072	0.060	0.110	0.159
	800	1.54	2.67	4.27	0.073	0.060	0.113	0.160
	1,600	1.59	2.72	4.32	0.071	0.059	0.113	0.160
Potassium chloride in a mixture of 50 per cent glycerol with ethyl alcohol.....	10	3.07	4.48	6.29	0.046	0.040	0.141	0.181
	50	3.54	5.21	7.38	0.047	0.042	0.167	0.217
	100	3.76	5.63	7.86	0.050	0.040	0.187	0.223
	200	4.09	5.94	8.37	0.045	0.041	0.185	0.243
	400	4.40	6.56	9.27	0.049	0.041	0.216	0.271
	800	4.52	6.76	9.61	0.049	0.042	0.224	0.295
	1,600	4.62	6.84	9.79	0.048	0.043	0.222	0.295
Potassium chloride in a mixture of 25 per cent glycerol with ethyl alcohol.....	10	7.26	9.31	11.94	0.028	0.028	0.205	0.263
	50	8.31	10.78	13.61	0.030	0.026	0.247	0.283
	100	9.29	12.15	15.39	0.031	0.027	0.286	0.324
	200	9.97	13.02	16.61	0.031	0.028	0.305	0.359
	400	11.32	15.31	19.15	0.035	0.025	0.399	0.384
	800	11.88	15.68	20.28	0.032	0.029	0.380	0.460
	1,600	12.37	16.31	21.06	0.032	0.028	0.394	0.475

TABLE 117.—Data for the Molecular Conductivity and Temperature Coefficients of Conductivity (at 25°, 35°, and 45°), in Per Cent and in Conductivity Units, for Potassium Chloride, Sodium Nitrate, Ammonium Bromide, and Strontium Chloride in the Various Mixtures of Glycerol with Water, Methyl Alcohol, and Ethyl Alcohol—Continued.

Salt.	V	Molecular conductivity.			Temperature coefficients.			
					Per cent.		Conductivity units.	
		$\mu_{25^\circ}$	$\mu_{35^\circ}$	$\mu_{45^\circ}$	25 to 35°	35 to 45°	25 to 35°	35 to 45°
Potassium chloride in a mixture of 75 per cent glycerol with methyl alcohol....	10	2.22	3.58	5.43	0.061	0.052	0.136	0.185
	50	2.41	3.93	5.91	0.063	0.050	0.152	0.198
	100	2.47	4.07	6.11	0.064	0.050	0.160	0.204
	200	2.58	4.21	6.38	0.063	0.051	0.163	0.217
	400	2.78	4.52	6.88	0.062	0.052	0.174	0.236
	800	2.83	4.64	7.07	0.064	0.052	0.181	0.243
	1,600	2.83	4.62	6.99	0.063	0.051	0.179	0.237
Potassium chloride in a mixture of 50 per cent glycerol with methyl alcohol....	10	8.10	11.09	14.54	0.037	0.031	0.299	0.345
	50	9.24	12.75	16.71	0.038	0.031	0.351	0.396
	100	9.59	13.17	17.48	0.037	0.033	0.358	0.431
	200	10.05	13.77	18.22	0.037	0.032	0.372	0.445
	400	11.04	15.20	20.17	0.038	0.032	0.416	0.497
	800	11.20	15.34	20.41	0.037	0.033	0.414	0.507
	1,600	11.38	15.63	20.64	0.036	0.032	0.425	0.501
Potassium chloride in a mixture of 25 per cent glycerol with methyl alcohol....	10	21.76	26.55	31.11	0.022	0.017	0.479	0.456
	50	25.85	31.45	37.75	0.022	0.020	0.560	0.630
	100	27.57	33.65	40.36	0.022	0.020	0.608	0.671
	200	28.72	35.34	42.30	0.023	0.020	0.662	0.696
	400	31.01	38.19	45.51	0.023	0.019	0.718	0.732
	800	33.15	50.70	48.85	0.023	0.020	0.755	0.815
	1,600	33.99	42.05	49.55	0.024	0.018	0.806	0.750
Sodium nitrate in a mixture of 75 per cent glycerol with water.....	10	4.88	7.46	10.80	0.053	0.045	0.258	0.334
	50	5.37	8.39	12.03	0.056	0.043	0.302	0.364
	100	5.45	8.44	12.33	0.055	0.046	0.299	0.389
	200	5.63	8.68	12.58	0.054	0.045	0.305	0.390
	400	6.09	9.35	13.65	0.053	0.046	0.326	0.430
	800	6.34	9.75	14.20	0.054	0.045	0.341	0.445
	1,600	6.37	9.75	14.34	0.053	0.047	0.338	0.459
Sodium nitrate in a mixture of 50 per cent glycerol with water.....	10	18.87	25.41	33.03	0.035	0.030	0.654	0.762
	50	20.60	27.84	36.08	0.035	0.030	0.724	0.824
	100	21.26	28.79	37.35	0.053	0.030	0.753	0.856
	200	21.46	29.34	37.98	0.037	0.029	0.788	0.864
	400	21.69	29.63	38.42	0.036	0.029	0.794	0.879
	800	23.73	31.74	42.17	0.034	0.033	0.801	1.043
	1,600	24.53	32.57	43.69	0.033	0.034	0.804	1.112
Sodium nitrate in a mixture of 25 per cent glycerol with water.....	10	48.19	60.40	73.81	0.025	0.022	1.221	1.341
	50	52.17	64.90	80.77	0.024	0.024	1.273	1.587
	100	53.65	68.25	82.75	0.027	0.021	1.460	1.450
	200	54.47	69.18	84.41	0.027	0.022	1.471	1.523
	400	55.25	69.74	86.03	0.026	0.023	1.449	1.629
	800	60.09	75.35	93.20	0.025	0.024	1.526	1.785
	1,600	62.03	77.90	96.30	0.025	0.023	1.587	1.840
Sodium nitrate in water.....	10	94.7	113.4	133.2	0.020	0.017	1.87	1.98
	50	103.8	125.0	147.5	0.020	0.018	2.12	2.25
	100	104.7	127.0	149.5	0.021	0.018	2.23	2.25
	200	107.8	130.5	153.2	0.021	0.017	2.27	2.27
	400	113.7	135.3	159.6	0.019	0.018	2.16	2.43
	800	113.0	135.8	160.1	0.020	0.018	2.28	2.43
	1,600	116.0	142.6	169.7	0.023	0.019	2.66	2.71

TABLE 117.—Data for the Molecular Conductivity and Temperature Coefficients of Conductivity (at 25°, 35°, and 45°), in Per Cent and in Conductivity Units, for Potassium Chloride, Sodium Nitrate, Ammonium Bromide, and Strontium Chloride in the Various Mixtures of Glycerol with Water, Methyl Alcohol, and Ethyl Alcohol—Continued.

Salt.	V	Molecular conductivity.			Temperature coefficients.			
					Per cent.		Conductivity units.	
		$\mu$ , 25°	$\mu$ , 35°	$\mu$ , 45°	25 to 35°	35 to 45°	25 to 35°	35 to 45°
Sodium nitrate in a mixture of 75 per cent glycerol with ethyl alcohol.....	10	1.02	1.77	2.79	0.074	0.058	0.075	0.102
	50	1.17	1.99	3.20	0.070	0.060	0.082	0.121
	100	1.20	2.09	3.30	0.074	0.058	0.089	0.121
	200	1.28	2.19	3.51	0.074	0.060	0.093	0.132
	400	1.38	2.37	3.75	0.072	0.058	0.099	0.138
	800	1.39	2.43	3.84	0.075	0.058	0.104	0.141
	1,600	1.39	2.42	3.87	0.074	0.060	0.103	0.145
Sodium nitrate in a mixture of 50 per cent glycerol with ethyl alcohol.....	10	3.08	4.49	6.20	0.046	0.038	0.141	0.171
	50	3.68	5.41	7.58	0.047	0.040	0.173	0.217
	100	3.89	5.74	8.07	0.047	0.041	0.185	0.233
	200	4.04	6.00	8.44	0.048	0.041	0.196	0.244
	400	4.52	6.67	9.49	0.047	0.042	0.215	0.282
	800	4.70	6.95	9.78	0.048	0.039	0.225	0.273
	1,600	4.80	7.14	10.18	0.049	0.043	0.234	0.304
Sodium nitrate in a mixture of 25 per cent glycerol with ethyl alcohol.....	10	7.36	9.45	11.74	0.028	0.024	0.209	0.229
	50	9.75	12.56	15.65	0.029	0.025	0.281	0.309
	100	10.57	13.65	17.33	0.029	0.027	0.308	0.368
	200	11.50	14.85	18.87	0.029	0.027	0.335	0.402
	400	12.89	16.85	21.34	0.030	0.027	0.396	0.449
	800	13.74	17.71	22.38	0.029	0.026	0.397	0.468
	1,600	14.00	18.36	22.72	0.030	0.024	0.436	0.436
Sodium nitrate in a mixture of 75 per cent glycerol with methyl alcohol....	10	1.86	2.99	4.54	0.060	0.052	0.113	0.155
	50	2.07	3.42	5.31	0.065	0.055	0.135	0.189
	100	2.17	3.58	5.43	0.065	0.052	0.141	0.185
	200	2.24	3.64	5.62	0.071	0.054	0.160	0.198
	400	2.41	3.99	6.02	0.065	0.051	0.158	0.203
	800	2.53	4.08	6.24	0.061	0.053	0.155	0.216
	1,600	2.49	4.13	6.26	0.066	0.051	0.164	0.213
Sodium nitrate in a mixture of 50 per cent glycerol with methyl alcohol....	10	7.35	10.02	13.25	0.036	0.031	0.267	0.323
	50	8.68	11.88	15.69	0.037	0.032	0.320	0.381
	100	9.09	12.53	16.47	0.038	0.031	0.344	0.394
	200	9.59	13.22	17.53	0.038	0.030	0.363	0.431
	400	10.44	14.46	19.06	0.038	0.032	0.402	0.460
	800	10.75	14.87	19.57	0.038	0.032	0.412	0.470
	1,600	10.80	15.08	19.57	0.039	0.029	0.428	0.449
Sodium nitrate in a mixture of 25 per cent glycerol with methyl alcohol...	10	20.77	25.22	30.59	0.021	0.021	0.445	0.537
	50	25.71	31.35	37.47	0.022	0.020	0.564	0.612
	100	27.59	33.81	40.31	0.022	0.020	0.622	0.650
	200	28.81	35.27	42.19	0.022	0.020	0.646	0.692
	400	30.06	36.88	44.45	0.022	0.020	0.682	0.757
	800	33.11	40.42	48.20	0.022	0.019	0.731	0.778
	1,600	34.00	41.82	49.78	0.023	0.019	0.782	0.796
Ammonium bromide in a mixture of 75 per cent glycerol with water.....	10	5.53	8.48	12.28	0.054	0.045	0.295	0.380
	50	5.91	9.14	13.26	0.055	0.045	0.323	0.412
	100	5.97	9.25	13.30	0.055	0.043	0.328	0.405
	200	6.17	9.54	13.83	0.055	0.045	0.337	0.429
	400	6.62	10.28	14.87	0.055	0.045	0.366	0.459
	800	6.95	10.81	15.45	0.055	0.043	0.386	0.464
	1,600	7.29	11.20	15.88	0.054	0.042	0.391	0.468



TABLE 117.—Data for the Molecular Conductivity and Temperature Coefficients of Conductivity (at 25°, 35°, and 45°), in Per Cent and in Conductivity Units, for Potassium Chloride, Sodium Nitrate, Ammonium Bromide, and Strontium Chloride in the Various Mixtures of Glycerol with Water, Methyl Alcohol, and Ethyl Alcohol—Continued.

Salt.	V	Molecular conductivity.			Temperature coefficients.			
					Per cent.		Conductivity units.	
		$\mu$ , 25°	$\mu$ , 35°	$\mu$ , 45°	25 to 35°	35 to 45°	25 to 35°	35 to 45°
Ammonium bromide in a mixture of 50 per cent glycerol with water.....	10	24.31	32.58	42.06	0.034	0.029	0.827	0.948
	50	25.74	34.54	44.59	0.031	0.029	0.880	1.005
	100	26.62	35.61	45.65	0.034	0.028	0.899	1.004
	200	27.01	36.12	46.44	0.033	0.028	0.911	1.032
	400	27.86	37.32	47.87	0.034	0.028	0.946	1.055
	800	30.20	40.54	52.33	0.034	0.029	1.034	1.179
	1,600	32.58	43.00	54.79	0.032	0.027	1.042	1.179
Ammonium bromide in a mixture of 25 per cent glycerol with water.....	10	61.45	76.93	92.72	0.025	0.020	1.548	1.579
	50	66.55	83.43	101.38	0.025	0.021	1.688	1.795
	100	67.68	84.90	103.56	0.025	0.022	1.722	1.866
	200	69.32	86.80	104.52	0.025	0.020	1.748	1.772
	400	70.69	88.08	106.74	0.024	0.021	1.739	1.866
	800	71.29	89.82	108.68	0.026	0.021	1.853	1.886
	1,600	71.34	89.58	107.96	0.025	0.020	1.824	1.836
Ammonium bromide in water.....	10	122.7	148.6	173.2	0.021	0.016	2.59	2.46
	50	131.4	158.2	185.8	0.020	0.017	2.68	2.76
	100	133.5	159.4	187.1	0.020	0.017	2.59	2.77
	200	135.3	163.8	191.1	0.021	0.017	2.85	2.73
	400	138.2	166.6	195.7	0.020	0.017	2.84	2.91
	800	142.0	170.7	199.3	0.020	0.017	2.87	2.86
	1,600	147.2	172.9	205.6	0.018	0.018	2.57	3.27
Ammonium bromide in a mixture of 75 per cent glycerol with ethyl alcohol.	10	1.32	2.25	3.55	0.070	0.058	0.093	0.130
	50	1.48	2.55	3.97	0.078	0.056	0.112	0.142
	100	1.50	2.59	4.11	0.072	0.058	0.109	0.152
	200	1.61	2.77	4.31	0.072	0.056	0.116	0.154
	400	1.55	2.62	4.23	0.075	0.061	0.117	0.161
	800	1.65	2.85	4.46	0.072	0.057	0.120	0.161
	1,600	1.67	2.82	4.50	0.070	0.059	0.115	0.168
Ammonium bromide in a mixture of 50 per cent glycerol with ethyl alcohol.	10	3.69	5.43	7.59	0.047	0.040	0.174	0.216
	50	4.30	6.28	8.77	0.046	0.040	0.198	0.249
	100	4.45	6.76	9.22	0.052	0.037	0.231	0.246
	200	4.68	6.90	9.72	0.047	0.040	0.222	0.282
	400	4.72	7.06	9.88	0.049	0.040	0.234	0.282
	800	5.02	7.48	10.45	0.049	0.039	0.246	0.297
	1,600	5.10	7.59	10.51	0.049	0.039	0.249	0.292
Ammonium bromide in a mixture of 25 per cent glycerol with ethyl alcohol.	10	8.51	10.85	13.39	0.026	0.024	0.234	0.254
	50	10.54	13.94	17.37	0.032	0.025	0.340	0.343
	100	11.45	14.81	18.59	0.029	0.025	0.336	0.378
	200	12.50	16.23	20.41	0.030	0.026	0.373	0.418
	400	12.94	16.87	21.23	0.030	0.026	0.393	0.436
	800	13.92	18.12	23.07	0.030	0.027	0.420	0.495
	1,600	14.38	18.91	24.05	0.031	0.027	0.453	0.514
Ammonium bromide in ethyl alcohol...	10	16.7	19.3	21.6	0.016	0.012	0.260	0.230
	50	23.8	27.3	30.9	0.015	0.013	0.350	0.360
	100	26.9	31.1	35.5	0.016	0.014	0.420	0.440
	200	29.8	34.7	39.8	0.016	0.014	0.490	0.510
	400	34.5	40.0	47.2	0.016	0.018	0.550	0.720
	800	37.6	44.2	51.0	0.018	0.015	0.660	0.680
	1,600	39.6	46.4	54.5	0.018	0.017	0.680	0.810

TABLE 117.—Data for the Molecular Conductivity and Temperature Coefficients of Conductivity (at 25°, 35°, and 45°), in Per Cent and in Conductivity Units, for Potassium Chloride, Sodium Nitrate, Ammonium Bromide, and Strontium Chloride in the Various Mixtures of Glycerol with Water, Methyl Alcohol, and Ethyl Alcohol—Continued.

Salt.	V	Molecular conductivity.			Temperature coefficients.			
					Per cent.		Conductivity units.	
		$\mu$ , 25°	$\mu$ , 35°	$\mu$ , 45°	25 to 35°	35 to 45°	25 to 35°	35 to 45°
Ammonium bromide in a mixture of 75 per cent glycerol with methyl alcohol	10	2.50	4.00	6.04	0.060	0.051	0.150	0.204
	50	2.70	4.42	6.91	0.064	0.056	0.172	0.249
	100	2.87	4.60	6.91	0.064	0.050	0.183	0.231
	200	2.94	4.79	7.23	0.063	0.051	0.185	0.244
	400	2.94	4.80	7.23	0.063	0.050	0.186	0.243
	800	3.05	5.01	7.53	0.064	0.050	0.196	0.252
	1,600	3.06	4.99	7.62	0.063	0.052	0.193	0.263
Ammonium bromide in a mixture of 50 per cent glycerol with methyl alcohol	10	9.66	13.03	16.86	0.035	0.029	0.337	0.383
	50	10.99	14.78	19.33	0.034	0.031	0.379	0.455
	100	11.33	15.44	21.13	0.036	0.037	0.411	0.569
	200	11.74	16.06	21.03	0.037	0.031	0.432	0.497
	400	11.99	16.43	21.59	0.037	0.031	0.444	0.516
	800	12.22	17.00	22.30	0.040	0.031	0.478	0.530
	1,600	12.63	17.48	22.90	0.038	0.031	0.485	0.542
Ammonium bromide in a mixture of 25 per cent glycerol with methyl alcohol	10	26.0	31.4	37.3	0.020	0.019	0.540	0.590
	50	30.1	36.5	43.9	0.021	0.020	0.640	0.740
	100	32.4	39.4	47.0	0.021	0.019	0.700	0.760
	200	33.7	41.1	49.7	0.022	0.021	0.740	0.860
	400	34.9	42.5	51.1	0.022	0.020	0.760	0.860
	800	36.4	44.3	53.1	0.022	0.020	0.790	0.880
	1,600	37.6	46.0	55.1	0.022	0.019	0.840	0.910
Ammonium bromide in methyl alcohol	10	59.1	65.4	73.0	0.011	0.012	0.630	0.760
	50	74.2	82.9	91.7	0.012	0.011	0.870	0.880
	100	79.5	90.3	99.5	0.013	0.010	1.080	0.920
	200	83.3	94.1	105.7	0.013	0.012	1.080	1.160
	400	89.3	98.5	111.5	0.010	0.013	0.920	1.300
	800	90.9	102.2	117.3	0.012	0.015	1.130	1.510
	1,600	93.4	105.0	118.3	0.012	0.013	1.160	1.330
Strontium chloride in glycerol	10	0.322	0.664	1.252	0.106	0.088	0.0342	0.0588
	50	0.403	0.840	1.558	0.108	0.085	0.0437	0.0718
	100	0.426	0.900	1.650	0.111	0.083	0.0474	0.0750
	200	0.452	0.958	1.777	0.112	0.085	0.0506	0.0819
	400	0.475	1.008	1.866	0.111	0.085	0.0533	0.0858
	800	0.483	1.037	1.934	0.115	0.086	0.0554	0.0897
	1,600	0.507	1.075	1.994	0.110	0.085	0.0568	0.0919
Strontium chloride in a mixture of 75 per cent glycerol with water	10	5.85	9.13	13.38	0.056	0.046	0.328	0.425
	50	6.90	10.82	16.08	0.056	0.048	0.392	0.526
	100	7.29	11.45	16.78	0.057	0.047	0.416	0.533
	200	7.76	12.34	18.07	0.059	0.047	0.458	0.573
	400	8.61	13.63	19.99	0.059	0.046	0.502	0.636
	800	9.21	14.56	21.23	0.058	0.046	0.535	0.667
	1,600	9.72	15.37	22.46	0.058	0.046	0.565	0.709
Strontium chloride in a mixture of 50 per cent glycerol with water	10	28.08	38.38	51.30	0.031	0.034	1.030	1.292
	50	33.35	45.12	59.31	0.036	0.031	1.177	1.419
	100	35.19	48.17	63.40	0.038	0.031	1.398	1.523
	200	36.84	50.59	66.13	0.037	0.031	1.375	1.554
	400	38.74	52.59	69.16	0.036	0.031	1.385	1.657
	800	42.03	56.88	74.78	0.035	0.031	1.485	1.790
	1,600	42.84	59.08	79.39	0.038	0.034	1.624	2.031

TABLE 117.—Data for the Molecular Conductivity and Temperature Coefficients of Conductivity (at 25°, 35°, and 45°), in Per Cent and in Conductivity Units, for Potassium Chloride, Sodium Nitrate, Ammonium Bromide, and Strontium Chloride in the Various Mixtures of Glycerol with Water, Methyl Alcohol, and Ethyl Alcohol—Continued.

Salt.	V	Molecular conductivity.			Temperature coefficients.			
					Per cent.		Conductivity units.	
		$\mu$ , 25°	$\mu$ , 35°	$\mu$ , 45°	25 to 35°	35 to 45°	25 to 35°	35 to 45°
Strontium chloride in a mixture of 25 per cent glycerol with water.....	10	79.7	100.5	122.3	0.026	0.022	2.08	2.18
	50	92.2	117.3	144.2	0.027	0.023	2.51	2.69
	100	97.7	122.9	152.2	0.026	0.024	2.52	2.93
	200	102.3	129.3	159.8	0.026	0.023	2.70	3.05
	400	103.8	133.0	163.0	0.028	0.022	2.92	3.00
	800	107.1	135.6	168.7	0.027	0.024	2.85	3.31
	1,600	109.2	137.3	170.2	0.026	0.024	2.81	3.29
Strontium chloride in water.....	10	175.3	210.6	247.8	0.020	0.018	3.53	3.72
	50	199.1	249.1	285.0	0.025	0.015	5.00	3.59
	100	207.5	252.5	299.1	0.021	0.015	4.50	4.66
	200	215.4	262.7	310.3	0.022	0.018	4.73	4.66
	400	224.5	274.8	323.8	0.022	0.017	5.03	4.90
	800	230.8	279.0	332.8	0.021	0.019	4.82	5.38
	1,600	235.9	285.6	342.9	0.021	0.020	4.97	5.73

TABLE 118.—Comparison of Temperature Coefficients in Various Mixtures from 25° to 35°.

Salt and solvent.	V	100 p. ct.	75 p. ct.	50 p. ct.	25 p. ct.	0 p. ct.
Ammonium bromide in mixtures of glycerol and water.....	10	0.103	0.054	0.034	0.025	0.021
	50	0.105	0.055	0.034	0.025	0.020
	100	0.107	0.055	0.034	0.025	0.020
	200	0.108	0.055	0.033	0.025	0.021
	400	0.107	0.055	0.034	0.024	0.020
	800	0.108	0.055	0.034	0.026	0.020
	1,600	0.111	0.054	0.032	0.025	0.018
Ammonium bromide in mixtures of glycerol and ethyl alcohol.....	10	0.103	0.070	0.047	0.026	0.016
	50	0.105	0.078	0.046	0.032	0.015
	100	0.107	0.072	0.052	0.029	0.016
	200	0.108	0.072	0.047	0.030	0.016
	400	0.107	0.075	0.049	0.030	0.016
	800	0.108	0.072	0.049	0.030	0.018
	1,600	0.111	0.070	0.049	0.031	0.018
Ammonium bromide in mixtures of glycerol and methyl alcohol.....	10	0.103	0.060	0.035	0.020	0.011
	50	0.105	0.064	0.034	0.021	0.012
	100	0.108	0.064	0.036	0.021	0.014
	200	0.107	0.063	0.037	0.022	0.013
	400	0.107	0.063	0.037	0.022	0.010
	800	0.108	0.064	0.040	0.022	0.012
	1,600	0.111	0.063	0.038	0.022	0.012
Sodium nitrate in mixtures of glycerol and water.....	10	0.103	0.053	0.035	0.025	0.020
	50	0.105	0.056	0.035	0.024	0.020
	100	0.110	0.055	0.035	0.027	0.021
	200	0.107	0.054	0.037	0.027	0.021
	400	0.106	0.053	0.036	0.026	0.019
	800	0.106	0.054	0.034	0.025	0.020
	1,600	0.106	0.053	0.033	0.025	0.023
Sodium nitrate in mixtures of glycerol and ethyl alcohol.....	10	0.103	0.074	0.046	0.028	.....
	50	0.105	0.070	0.047	0.029	.....
	100	0.107	0.074	0.047	0.029	.....
	200	0.110	0.074	0.048	0.029	.....
	400	0.106	0.072	0.047	0.030	.....
	800	0.106	0.075	0.048	0.029	.....
	1,600	0.107	0.074	0.049	0.030	.....

TABLE 118.—Comparison of Temperature Coefficients in Various Mixtures from 25° to 35°—Con.

Salt and solvent.	V	100 p. ct.	75 p. ct.	50 p. ct.	25 p. ct.	0 p. ct.
Sodium nitrate in mixtures of glycerol and methyl alcohol.....	10	0.103	0.060	0.036	0.021	.....
	50	0.105	0.065	0.037	0.022	.....
	100	0.107	0.065	0.038	0.022	.....
	200	0.110	0.067	0.038	0.022	.....
	400	0.106	0.065	0.038	0.022	.....
	800	0.106	0.061	0.038	0.022	.....
	1,600	0.106	0.066	0.039	0.023	.....
Potassium chloride in mixtures of glycerol and water.....	10	0.101	0.055	0.034	0.025	0.019
	50	0.107	0.056	0.034	0.026	0.019
	100	0.105	0.055	0.034	0.024	0.020
	200	0.105	0.055	0.034	0.025	0.019
	400	0.095	0.055	0.034	0.024	0.020
	800	0.096	0.055	0.034	0.024	0.020
	1,600	0.071	0.056	0.034	0.025	0.021
Potassium chloride in mixtures of glycerol and ethyl alcohol.....	10	0.101	0.069	0.046	0.028	.....
	50	0.107	0.072	0.047	0.030	.....
	100	0.105	0.073	0.050	0.031	.....
	200	0.105	0.072	0.045	0.031	.....
	400	0.095	0.072	0.049	0.035	.....
	800	0.096	0.073	0.049	0.032	.....
	1,600	0.071	0.071	0.048	0.032	.....
Potassium chloride in mixtures of glycerol and methyl alcohol.....	10	0.101	0.061	0.037	0.022	.....
	50	0.107	0.063	0.038	0.022	.....
	100	0.105	0.064	0.037	0.022	.....
	200	0.105	0.063	0.037	0.023	.....
	400	0.095	0.062	0.038	0.023	.....
	800	0.096	0.064	0.037	0.022	.....
	1,600	0.071	0.063	0.036	0.024	.....
Strontium chloride in mixtures of glycerol and water.....	10	0.106	0.056	0.031	0.026	0.020
	50	0.108	0.056	0.036	0.027	0.025
	100	0.111	0.057	0.038	0.026	0.021
	200	0.112	0.059	0.037	0.026	0.022
	400	0.111	0.059	0.036	0.028	0.022
	800	0.115	0.058	0.035	0.027	0.021
	1,600	0.110	0.058	0.038	0.026	0.021

TABLE 119.—Viscosities and Fluidities of Solutions in Glycerol at 25°, 35°, and 45°.

Salt.	$\eta$ 25°	$\eta$ 35°	$\eta$ 45°	$\theta$ 25°	$\theta$ 35°	$\theta$ 45°	Temperature coefficients.	
							25 to 35°	35 to 45°
KCl.....	6.362	2.836	1.399	0.1571	0.3527	0.7147	0.124	0.103
KBr.....	6.197	2.760	1.376	0.1613	0.3623	0.7264	0.124	0.101
KNO <sub>3</sub> .....	6.065	2.734	1.353	0.1648	0.3659	0.7391	0.122	0.099
NaCl.....	6.716	2.920	1.445	0.1613	0.3429	0.7143	0.124	0.106
NaBr.....	6.439	2.865	1.400	0.1553	0.3490	0.7143	0.124	0.106
NaI.....	6.303	2.822	1.409	0.1586	0.3543	0.7105	0.124	0.101
NaNO <sub>3</sub> .....	6.288	2.803	1.405	0.1590	0.3546	0.7117	0.123	0.101
NH <sub>4</sub> Cl.....	6.142	2.741	1.360	0.1628	0.3649	0.7357	0.124	0.101
NH <sub>4</sub> Br.....	5.970	2.681	1.329	0.1672	0.3729	0.7524	0.123	0.102
NH <sub>4</sub> NO <sub>3</sub> .....	6.306	2.800	1.408	0.1587	0.3572	0.7097	0.124	0.099
BaCl <sub>2</sub> .....	7.447	3.288	1.626	0.1343	0.3041	0.6150	0.126	0.102
BaBr <sub>2</sub> .....	7.100	3.199	1.571	0.1409	0.3126	0.6366	0.122	0.103
Ba(NO <sub>3</sub> ) <sub>2</sub> .....	7.212	3.182	1.571	0.1387	0.3143	0.6516	0.126	0.107
SrCl <sub>2</sub> .....	7.336	3.224	1.589	0.1363	0.3104	0.6291	0.127	0.103
SrBr <sub>2</sub> .....	7.337	3.219	1.574	0.1365	0.3107	0.6354	0.127	0.104
Sr(NO <sub>3</sub> ) <sub>2</sub> .....	7.640	3.335	1.640	0.1308	0.2998	0.6098	0.129	0.106
CaBr <sub>2</sub> .....	7.674	3.373	1.630	0.1303	0.2964	0.6135	0.127	0.106
Ca(NO <sub>3</sub> ) <sub>2</sub> .....	7.411	3.278	1.617	0.1350	0.3050	0.6184	0.125	0.103
Solvent.....	6.067	2.761	1.352	0.1648	0.3683	0.7396	0.124	0.101

TABLE 120.—Viscosities and Fluidities of Solutions in Glycerol at 55°, 65°, and 75°.

Salt.	$\eta$ 55°	$\eta$ 65°	$\eta$ 75°	$\theta$ 55°	$\theta$ 65°	$\theta$ 75°	Temperature coefficients.	
							55 to 65°	65 to 75°
KCl.....	0.7435	0.4353	0.2648	1.345	2.297	3.776	0.071	0.064
KBr.....	0.7475	0.4353	0.2709	1.338	2.297	3.692	0.065	0.061
NaBr.....	0.7664	0.4439	0.2689	1.305	2.253	3.719	0.072	0.065
NH <sub>4</sub> Cl.....	0.7366	0.4260	0.2613	1.357	2.342	3.827	0.072	0.063
NH <sub>4</sub> NO <sub>3</sub> .....	0.7284	0.4254	0.2618	1.373	2.351	3.819	0.071	0.062
CoCl <sub>2</sub> .....	0.8225	0.4762	0.2884	1.215	2.099	3.467	0.073	0.065
SrCl <sub>2</sub> .....	0.8536	0.4932	0.2981	1.172	2.028	3.355	0.073	0.065
Solvent.....	0.7415	0.4288	0.2620	1.350	2.331	3.817	0.072	0.063

TABLE 121.—Viscosities and Fluidities of Solutions in Mixtures of Glycerol with Water at 25°, 35°, and 45°

Solvent.	Salt.	$\eta$ 25°	$\eta$ 35°	$\eta$ 45°	$\theta$ 25°	$\theta$ 35°	$\theta$ 45°	Temperature coefficients.	
								25-35°	35-45°
In glycerol.....	KCl	6.362	2.836	1.399	0.1571	0.3527	0.7147	0.124	0.103
	NH <sub>4</sub> Br	5.970	2.681	1.329	0.1672	0.3729	0.7524	0.123	0.102
	NaNO <sub>3</sub>	6.288	2.803	1.405	0.1590	0.3546	0.7117	0.123	0.101
	SrCl <sub>2</sub>	7.336	3.224	1.589	0.1363	0.3104	0.6291	0.127	0.103
	Solvent	6.067	2.761	1.352	0.1648	0.3683	0.7396	0.124	0.101
In 75 per cent glycerol with water.....	KCl	0.3394	0.2003	0.1293	2.943	4.993	7.733	0.0698	0.0549
	NH <sub>4</sub> Br	0.3278	0.1932	0.1249	3.035	5.176	8.008	0.0699	0.0547
	NaNO <sub>3</sub>	0.3274	0.1947	0.1233	3.054	5.137	8.111	0.0682	0.0558
	SrCl <sub>2</sub>	0.3642	0.2179	0.1326	2.746	4.696	7.543	0.0713	0.0606
	Solvent	0.3169	0.1884	0.1186	3.156	5.307	8.431	0.0681	0.0586
In 50 per cent glycerol with water.....	KCl	0.06481	0.04385	0.03187	15.27	22.82	31.37	0.0422	0.0347
	NH <sub>4</sub> Br	0.06085	0.04251	0.03102	16.43	23.52	32.05	0.0431	0.0321
	NaNO <sub>3</sub>	0.06333	0.04372	0.03216	15.79	22.87	31.10	0.0447	0.0363
	SrCl <sub>2</sub>	0.06607	0.04563	0.03335	15.13	21.90	29.99	0.0379	0.0369
	Solvent	0.06109	0.04233	0.03114	16.37	23.63	32.10	0.0438	0.0358
In 25 per cent glycerol with water.....	KCl	0.02054	0.01546	0.01246	48.68	64.67	80.25	0.0328	0.0242
	NH <sub>4</sub> Br	0.02046	0.01552	0.01226	48.88	64.50	81.56	0.0320	0.0264
	NaNO <sub>3</sub>	0.02086	0.01556	0.01235	47.95	64.28	80.96	0.0340	0.0245
	SrCl <sub>2</sub>	0.02145	0.01614	0.01277	46.62	61.97	78.31	0.0329	0.0263
	Solvent	0.01946	0.01466	0.01171	51.38	68.22	85.45	0.0327	0.0253
In water.....	KCl	0.00902	0.00729	0.00608	110.8	137.0	164.6	0.0243	0.0201
	NH <sub>4</sub> Br	0.00894	0.00722	0.00609	112.0	138.6	164.1	0.0246	0.0199
	NaNO <sub>3</sub>	0.00903	0.00732	0.00608	110.8	136.6	164.4	0.0236	0.0202
	SrCl <sub>2</sub>	0.00927	0.00749	0.00628	107.9	133.5	159.4	0.0237	0.0194
	Solvent	0.00891	0.00720	0.00598	112.2	138.9	167.2	0.0237	0.0204

TABLE 122.—Viscosities and Fluidities of Solutions in Mixtures of Glycerol with Ethyl Alcohol at 25°, 35°, and 45°.

Solvent.	Salt.	$\eta_{25^\circ}$	$\eta_{35^\circ}$	$\eta_{45^\circ}$	$\theta_{25^\circ}$	$\theta_{35^\circ}$	$\theta_{45^\circ}$	Temperature coefficients.	
								25–35°	35–45°
In 75 per cent glycerol with ethyl alcohol	KCl	1.123	0.5942	0.3387	0.8904	1.683	2.952	0.0890	0.0754
	NH <sub>4</sub> Br	1.085	0.5762	0.3291	0.9214	1.736	3.039	0.0885	0.0751
	NaNO <sub>3</sub>	1.171	0.6185	0.3509	0.8547	1.635	2.850	0.0900	0.0762
	Solvent	1.029	0.5404	0.3111	0.9720	1.830	3.215	0.0912	0.0759
In 50 per cent glycerol with ethyl alcohol	KCl	0.2175	0.1377	0.08840	4.598	7.381	11.31	0.0605	0.0533
	NH <sub>4</sub> Br	0.2163	0.1325	0.08668	4.731	7.550	11.54	0.0595	0.0528
	NaNO <sub>3</sub>	0.2213	0.1360	0.08906	4.523	7.353	11.23	0.0620	0.0527
	Solvent	0.2123	0.1351	0.08723	4.712	7.402	11.46	0.0600	0.0529
In 25 per cent glycerol with ethyl alcohol	KCl	0.044730	0.03263	0.02487	22.36	30.66	40.21	0.0371	0.0311
	NH <sub>4</sub> Br	0.043960	0.03227	0.02442	22.75	31.01	40.94	0.0369	0.0326
	NaNO <sub>3</sub>	0.044640	0.03276	0.02481	22.40	30.52	40.31	0.0362	0.0320
	Solvent	0.041840	0.03061	0.02303	23.90	32.77	43.42	0.0371	0.0324
In ethyl alcohol	NH <sub>4</sub> Br	0.012160	0.009526	0.007979	86.13	105.1	125.3	0.0219	0.0193
	Solvent	0.010680	0.008683	0.007292	93.70	115.2	137.7	0.0227	0.0191

TABLE 123.—Viscosities and Fluidities of Solutions in Mixtures of Glycerol with Methyl Alcohol at 25°, 35°, and 45°.

Solvent.	Salt.	$\eta_{25^\circ}$	$\eta_{35^\circ}$	$\eta_{45^\circ}$	$\theta_{25^\circ}$	$\theta_{35^\circ}$	$\theta_{45^\circ}$	Temperature coefficients.	
								25 to 35°	35 to 45°
In 75 per cent glycerol with methyl alcohol	KCl	0.6308	0.3512	0.2129	1.585	2.850	4.696	0.0797	0.0659
	NH <sub>4</sub> Br	0.5999	0.3347	0.2011	1.666	2.987	4.973	0.0793	0.0665
	NaNO <sub>3</sub>	0.6362	0.3590	0.2122	1.572	2.786	4.713	0.0771	0.0689
	Solvent	0.6242	0.3519	0.2087	1.609	2.842	4.792	0.0763	0.0681
In 50 per cent glycerol with methyl alcohol	KCl	0.09521	0.06367	0.04474	10.51	15.70	22.35	0.0494	0.0423
	NH <sub>4</sub> Br	0.09225	0.06300	0.04361	10.84	15.87	22.93	0.0464	0.0444
	NaNO <sub>3</sub>	0.09717	0.06502	0.04574	10.29	15.74	21.87	0.0496	0.0436
	Solvent	0.09657	0.06512	0.04446	10.35	15.35	22.50	0.0484	0.0468
In 25 per cent glycerol with methyl alcohol	KCl	0.02063	0.01631	0.0131	48.02	61.32	76.31	0.0276	0.0244
	NH <sub>4</sub> Br	0.02064	0.01610	0.0130	48.46	62.11	76.01	0.0261	0.0223
	NaNO <sub>3</sub>	0.02098	0.01627	0.0130	47.75	61.48	76.46	0.0287	0.0243
	Solvent	0.01886	0.01481	0.0119	53.01	67.53	83.71	0.0274	0.0240
In methyl alcohol	NH <sub>4</sub> Br	0.006254	0.005410	0.004745	159.9	184.8	211.2	0.0155	0.0143
	Solvent	0.005842	0.005066	0.004469	171.2	197.4	223.7	0.0157	0.0139

TABLE 124.—Viscosities and Fluidities of Substances which were Found to Lower the Viscosity of Pure Glycerol at 25°, 35°, and 45°.

Salt.	V	$\eta_{25^\circ}$	$\eta_{35^\circ}$	$\eta_{45^\circ}$	$\theta_{25^\circ}$	$\theta_{35^\circ}$	$\theta_{45^\circ}$	Temperature coefficients.	
								25 to 35°	35 to 45°
NaNO <sub>3</sub>	0.10	5.367	2.425	1.222	0.1863	0.4125	0.8186	0.121	0.100
NH <sub>4</sub> Br	0.10	5.206	2.329	1.187	0.1929	0.4264	0.8423	0.121	0.098
NH <sub>4</sub> Br	0.50	5.071	2.324	1.189	0.1972	0.4302	0.8409	0.118	0.096
NH <sub>4</sub> I	0.10	5.108	2.320	1.165	0.1957	0.4308	0.8583	0.118	0.098
NH <sub>4</sub> I	0.50	4.605	2.157	1.060	0.2173	0.4745	0.9259	0.118	0.096
RbBr	0.10	5.183	2.332	1.176	0.1975	0.4288	0.8502	0.117	0.098
RbBr	0.50	4.768	2.183	1.112	0.2098	0.4583	0.8998	0.118	0.096
Solvent	.....	5.298	2.366	1.198	0.1888	0.4226	0.8347	0.118	0.097

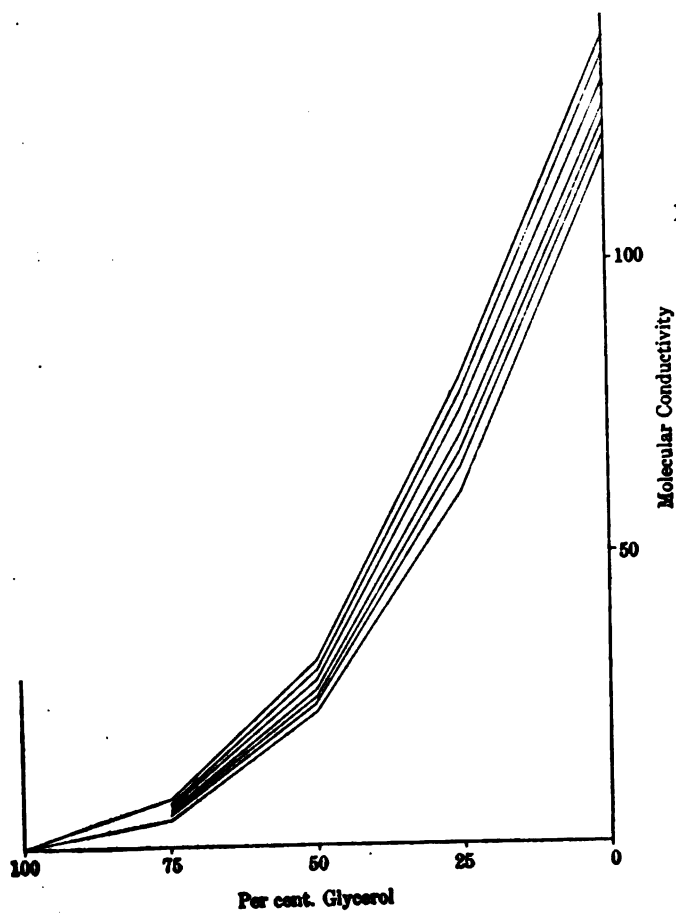
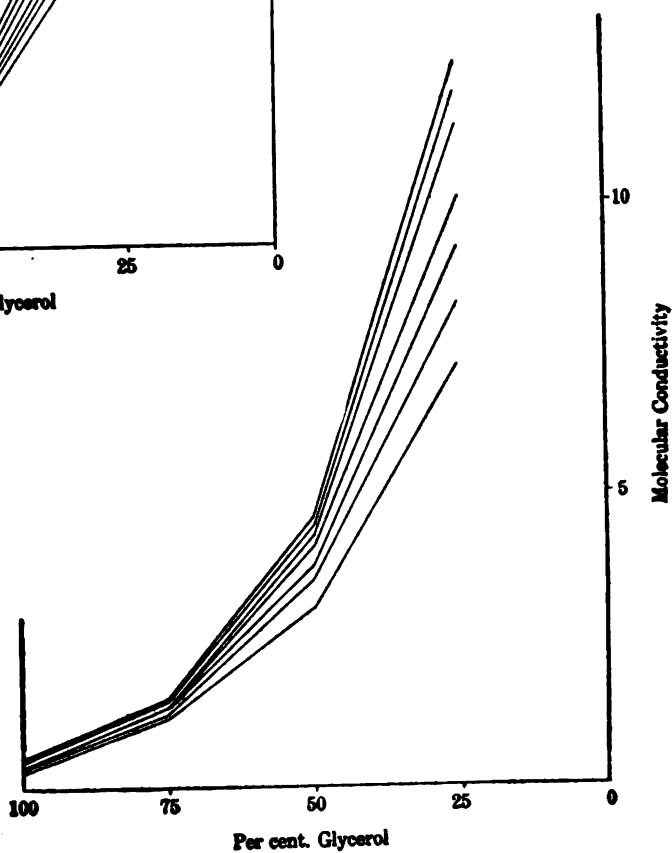


FIG. 70.—Conductivity of Potassium Chloride in Glycerol-Water at 25°.

FIG. 71.—Conductivity of Potassium Chloride in Glycerol-Ethyl Alcohol at 25°.



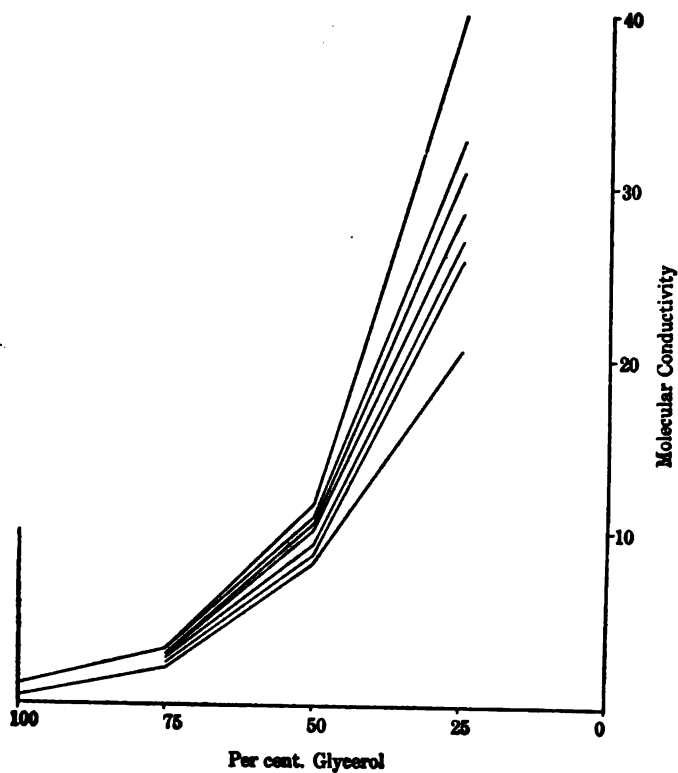


FIG. 72.—Conductivity of Potassium Chloride in Glycerol-Methyl Alcohol at 25°.

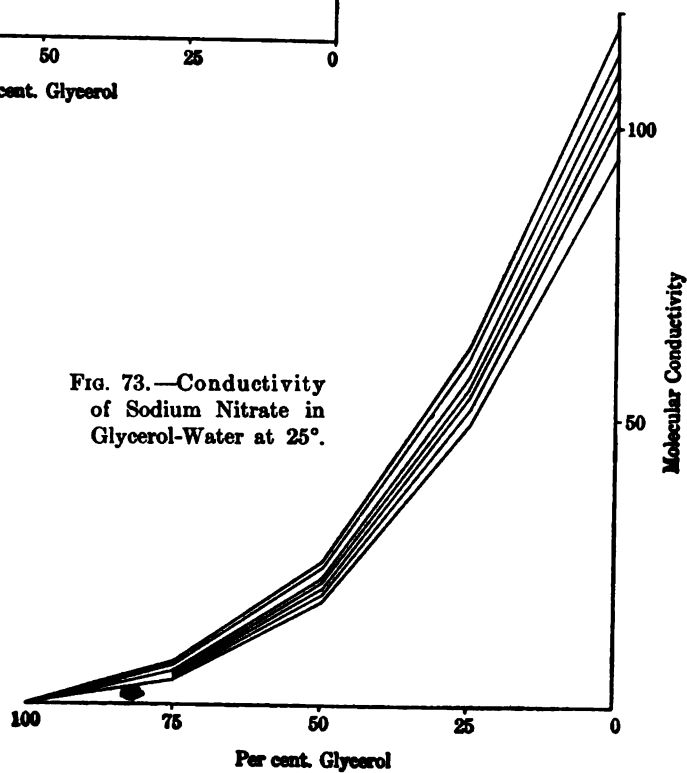


FIG. 73.—Conductivity of Sodium Nitrate in Glycerol-Water at 25°.



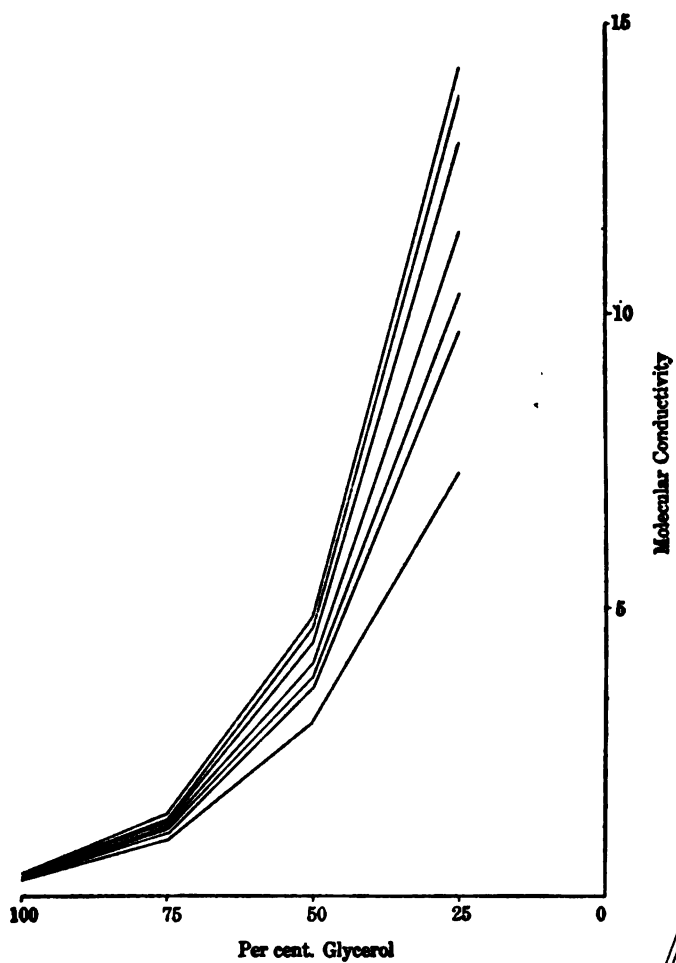
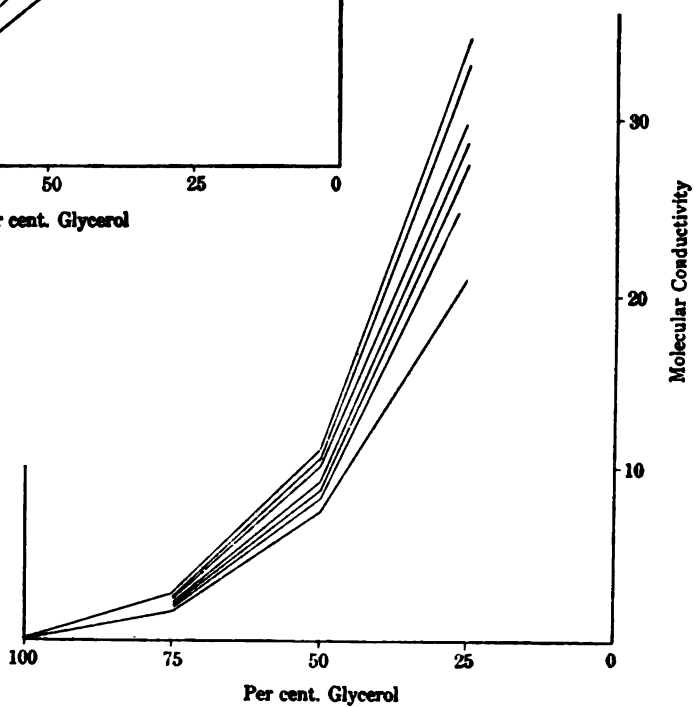


FIG. 74.—Conductivity of Sodium Nitrate in Glycerol-Ethyl Alcohol at 25°.

FIG. 75.—Conductivity of Sodium Nitrate in Glycerol-Methyl Alcohol at 25°.



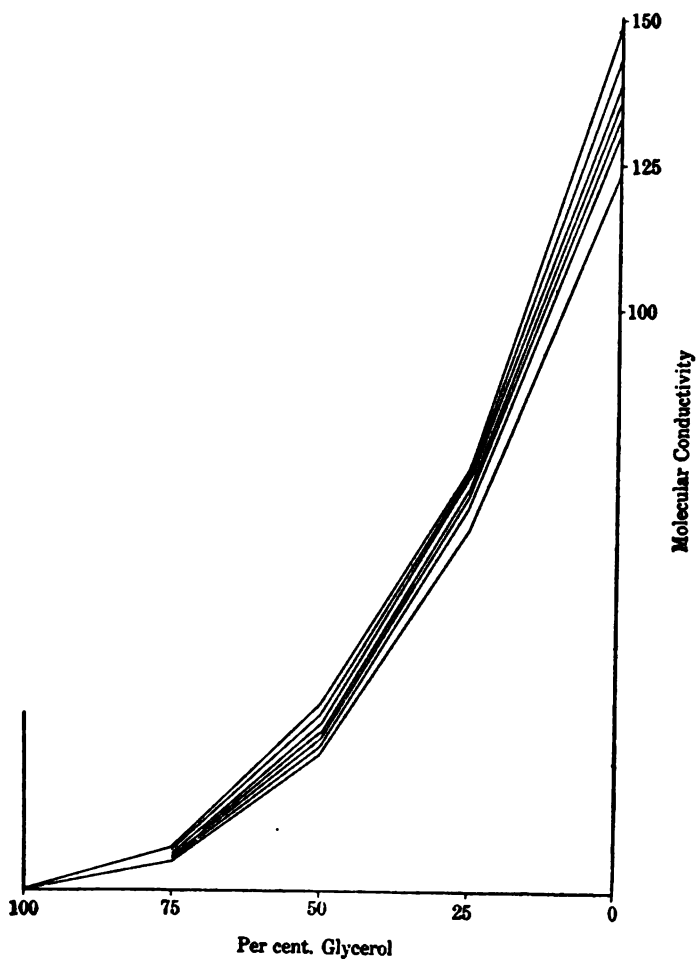
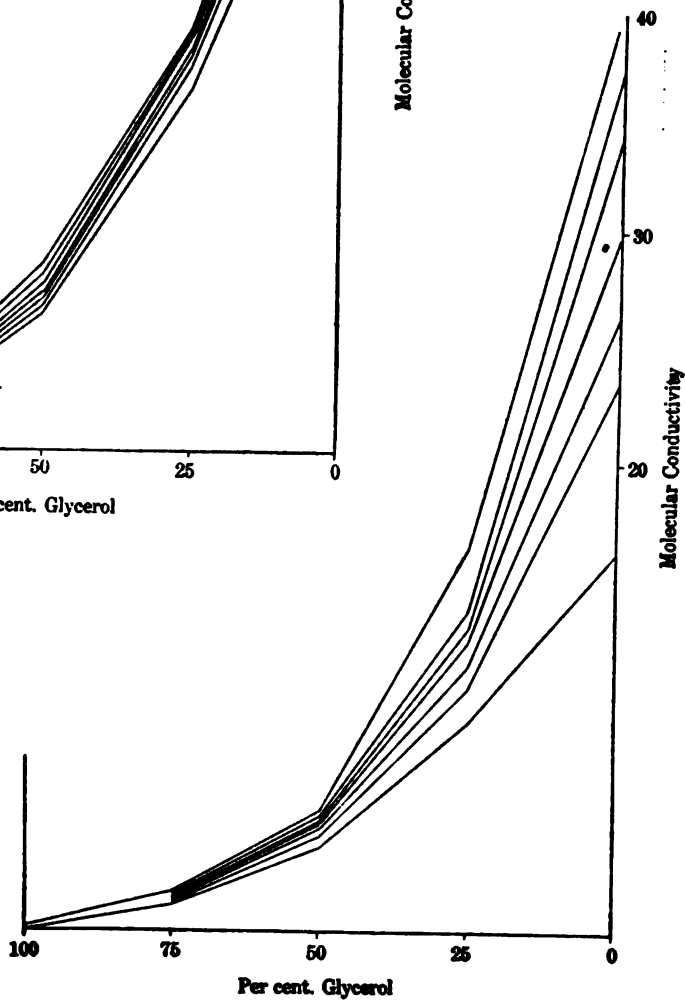


FIG. 76.—Conductivity of Ammonium Bromide in Glycerol-Water at 25°.

FIG. 77.—Conductivity of Ammonium Bromide in Glycerol-Ethyl Alcohol at 25°.



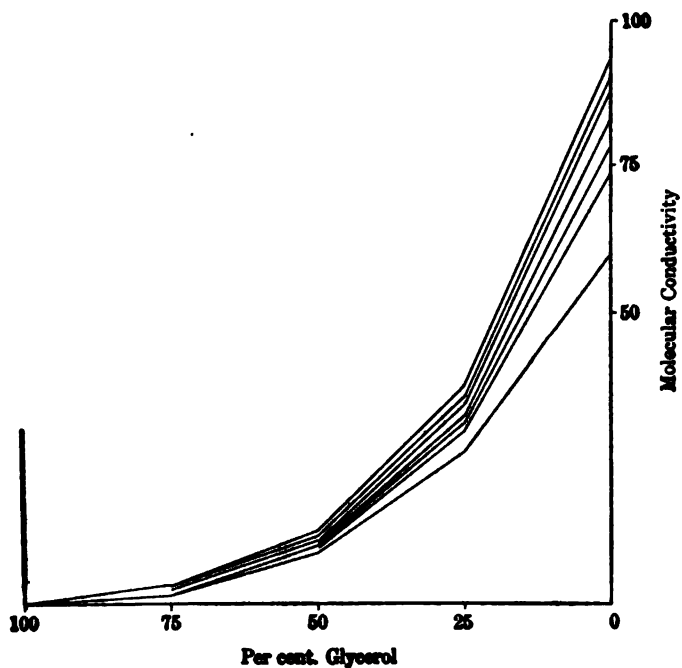
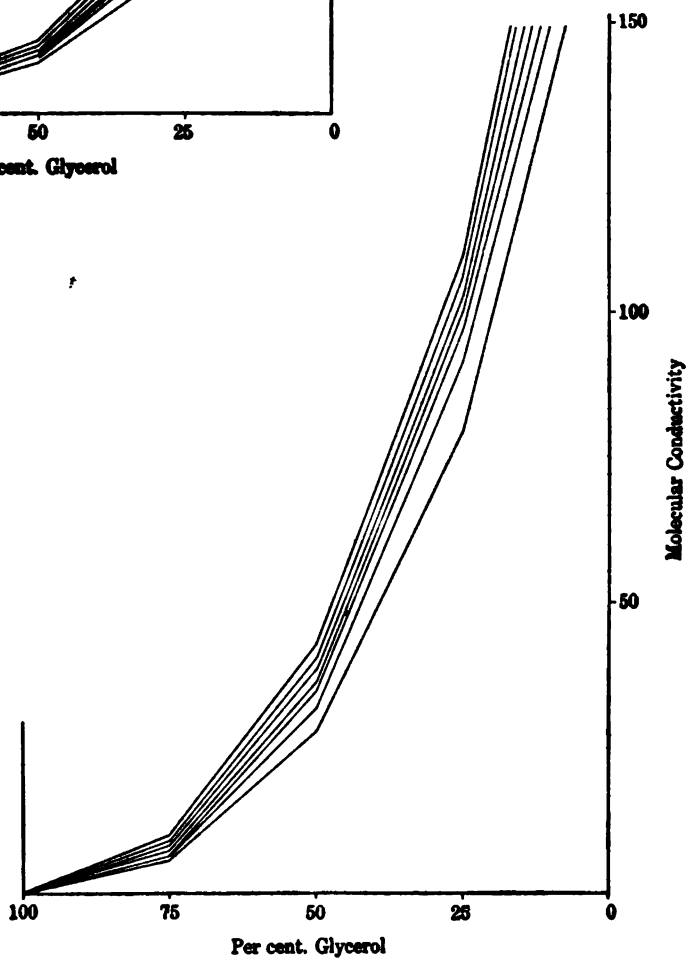


FIG. 78.—Conductivity of Ammonium Bromide in Glycerol-Methyl Alcohol at 25°.

FIG. 79.—Conductivity of Strontium Chloride in Glycerol-Water at 25°.



## DISCUSSION OF RESULTS.

A rise in temperature causes an increase in conductivity, which may be due to either or to both of the following causes: first, an increase in the number of the ions present, and second, an increase in the velocity of the ions. That the number of the ions does not generally increase with rise in temperature has been shown by direct measurement of the degree of dissociation by means of the conductivity method.

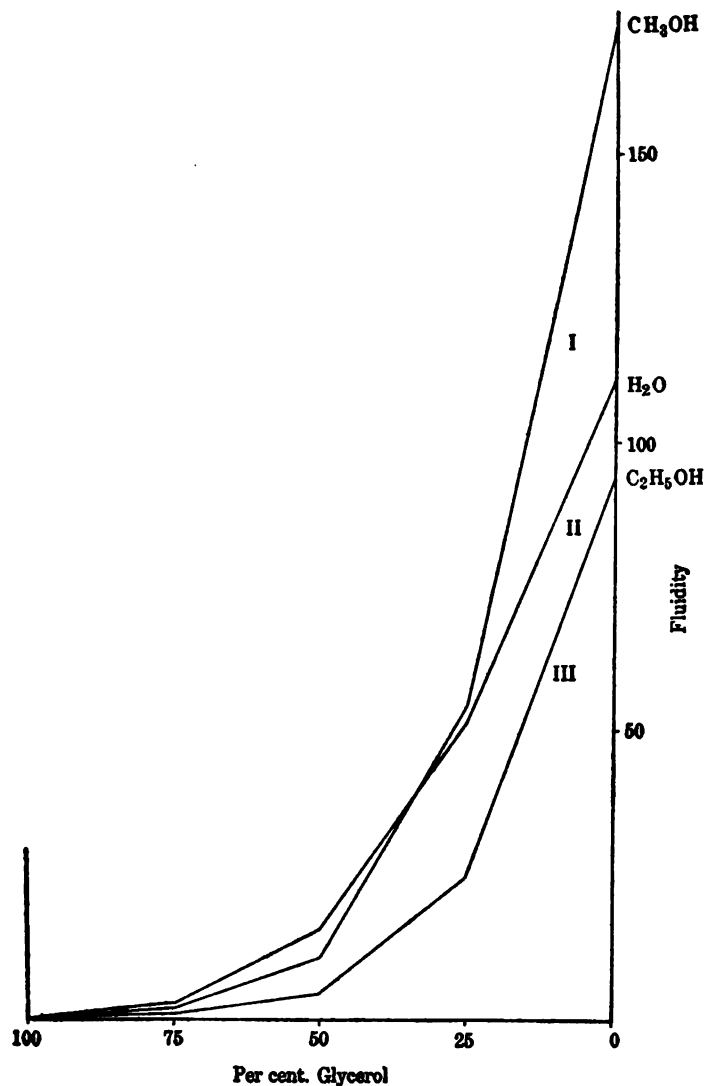


FIG. 80.—Fluidity of Glycerol Mixtures at 25°.

This is in accord with the theory of Dutoit and Aston, which makes the dissociating power of a solvent a function of its own association. The degree of association of a solvent has been shown by the method of Ramsay and Shields to decrease with rise

in temperature; hence, its power to dissociate an electrolyte into its ions has been diminished. It is, however, true that the theory of Dutoit and Aston is only an approximation.

The decrease in velocity of the ions with rise in temperature must then be the one conditioning cause of increase in conductivity. This change in velocity of the ions may be due to either or to both of the following causes: First, change in the viscosity of the medium through which the ions move; second, as Jones<sup>1</sup> and his coworkers have shown, to the change in complexity of the solvates which surround the ions.

In no other solvent is the change in conductivity with change in temperature so pronounced as in the one which chiefly concerns this investigation, viz, glycerol. The chief cause of this change is largely the change in the viscosity of the solution, while we believe that there is some evidence brought out in this investigation that indicates the presence of glycerolates.

Table 115 gives the molecular conductivities at 25°, 35°, and 45° of all the electrolytes which we have studied in pure glycerol as a solvent. It is seen that in all cases the values for  $\mu$ , are extremely small, but show, in general, a regular increase, both with increased dilution and with rise in temperature.

Associated with the conductivity of every substance are the temperature coefficients of conductivity, both in per cent and in conductivity units. Since the latter show the actual increase in conductivity per degree rise in temperature, a discussion of these data will bring out the most interesting points of this part of the work.

Although the temperature coefficients of conductivity, when expressed in conductivity units, show, in general, a regular increase with increased dilution, this is much more marked with ternary than with binary electrolytes. This fact has been observed by Jones for aqueous solutions in a discussion of the work of West.<sup>2</sup>

Results of the present investigation show that in glycerol the temperature coefficients of conductivity of any given substance, at high dilution, are larger than at lower dilution, and that the relative increase is greater with salts of barium, strontium, calcium, and cobalt than with salts of sodium, potassium, and ammonium. These facts may be explained in terms of the theory of solvation. That solvation takes place in aqueous solution has been shown beyond reasonable doubt by Jones and his coworkers; and, indeed, Jones and Strong have obtained abundant spectroscopic evidence for solvates in glycerol as a solvent.

If there is solvation, then, according to the mass law, in the more dilute solutions, where the amount of solvate per ion is greatest, we should expect to find the most complex solvates. Any change in temperature would produce the greatest effect where the solvation was greatest, that is, in the most dilute solutions. Again, this change in solvation should be more apparent in those salts which have the greater power of combining with the solvent, or, in the case of water, with those salts that have the largest number of molecules of water of crystallization.

We can not, of course, say that salts of barium, strontium, calcium, and cobalt possess a power of combining with glycerol similar to that which they manifest towards water, but it is not surprising to find solvation more marked with these salts than with salts that have very slight hydrating power, such as the salts of sodium, potassium, and ammonium.

<sup>1</sup>Amer. Chem. Jour., 35, 445 (1906).

<sup>2</sup>*Ibid.*, 34, 357 (1905).

It is also true that salts of approximately the same hydrating power show, in glycerol, temperature coefficients of the same order of magnitude.

The molecular conductivities at low dilutions in nearly every case are smaller for ternary than for binary electrolytes, while at higher dilutions the reverse is true without exception. This may be due to the fact that glycerol is only a fair dissociating agent, resembling methyl and ethyl alcohols, and has, at moderate concentrations, the power of producing only two ions from a ternary electrolyte, or at least dissociating a ternary electrolyte only to a moderate extent.

We should expect to find the ternary electrolytes yielding more ions at higher dilutions, and, hence, showing a greater molecular conductivity than binary electrolytes under the same conditions. That this is true may be best shown by comparing the molecular conductivities of several of the binary and ternary electrolytes used.

In table 125 the molecular conductivities of several typical salts at 25° are compared at volumes 10 and 1,600, respectively. These data confirm the above statement that while at low dilutions a ternary electrolyte usually has the smaller molecular conductivity, at higher dilutions the reverse is usually true.

TABLE 125.—*Molecular Conductivities of Several Salts.*

Salt	$\mu, 10$	$\mu, 1600$
KNO <sub>3</sub> .....	0.337	0.431
KBr.....	0.366	0.413
NaCl.....	0.328	0.395
BaBr <sub>2</sub> .....	0.330	0.530
Ba(NO <sub>3</sub> ) <sub>2</sub> .....	0.246	0.462
Ca(NO <sub>3</sub> ) <sub>2</sub> .....	0.283	0.472
SrCl <sub>2</sub> .....	0.322	0.507

Table 116 gives the molecular conductivities and temperature coefficients of conductivity of all the salts studied at 55°, 65°, and 75°. The same general relations hold at these temperatures as at the lower temperatures, viz, a regular increase in conductivity with increased dilution and rise in temperature; and a more marked increase, or a larger temperature coefficient, with those salts which in aqueous solutions possess the greatest power of hydration. The same reasoning employed above for the lower temperatures is applicable here.

Table 117 contains the data for the molecular conductivity and temperature coefficients of conductivity, at 25°, 35°, and 45°, in per cent and in conductivity units, for potassium chloride, sodium nitrate, ammonium bromide, and strontium chloride in the various mixtures of glycerol with water, methyl alcohol, and ethyl alcohol. The results are plotted in figs. 70 to 79, inclusive.

These curves show that the conductivities in such mixtures do not follow the law of averages, but are always less. In every case there is a marked sagging of the curves, but in no instance was a minimum obtained. This deviation from the law of averages has been explained by the work of Jones with Lindsay and Murray. When glycerol is mixed with water, or with either of the alcohols, it is clear that the properties of the mixture are not additive, the one solvent tending to lessen the association of the other; and, hence, their combined power of dissociating electrolytes is less than would be expected if there were no such lowering of each other's association.

Potassium chloride and sodium nitrate are nearly insoluble in the alcohols, and yet curves expressing the conductivities of these salts in mixtures of the alcohols with glycerol are strikingly similar to those of ammonium bromide. This seems to indicate that the deviation from the law of averages is due largely to the change in association of the glycerol.

Table 118 gives a comparison of the percentage temperature coefficients of conductivity from 25° to 35° of all the salts we have studied in mixed solvents. In pure glycerol these values are very large, from 10 to 11 per cent per degree rise in temperature. They decrease very rapidly with the addition of either water or the alcohols. The temperature coefficients also decrease very rapidly with rise in temperature.

#### VISCOSITIES AND FLUIDITIES.

Table 119 includes the viscosities and fluidities of the eighteen electrolytes whose conductivities we have studied. Measurements were made only with the tenth-normal solutions, since, at higher dilutions, the difference in viscosity between the solution and solvent is hardly large enough to be detected, much less measured. In nearly every case the viscosity of the solution is greater than that of the solvent. Ammonium bromide was found to be an exception to this rule, and will be discussed more fully. The temperature coefficients of fluidity are very large, being somewhat greater than the temperature coefficients of conductivity. That the former are larger than the latter is not surprising, since rise in temperature would decrease the dissociation and thus decrease the conductivity, which would, at least in part, offset the increase in conductivity caused by increase in fluidity.

The ternary electrolytes show a much greater increase in viscosity than the binary electrolytes. It will be recalled that the salts which show the greatest increase in viscosity are those in which the solvation seemed to be the greatest.

This increase in viscosity of the ternary over the binary electrolytes may be due to several causes. There may be a greater number of ions present, which, since the viscosity is a function of the skin friction, would increase the viscosity; or the molecules of the solvent, combined as solvates, may be so attached to the molecule of the solute as to hinder its movement. It is not supposed that in any case of solvation the molecules of the solvent are held so as to form a complex chemical molecule, as this would, of course, decrease skin friction and thus lessen the viscosity of the solution.

The fact that solutions of ternary electrolytes show greater viscosities than solutions of binary electrolytes may be a conditioning factor in the small molecular conductivity shown by them in the more concentrated solutions. It is, however, hardly possible that this could account entirely for the phenomenon, since there is probably less actual dissociation of a ternary than of a binary electrolyte in the most concentrated solutions.

It is probable, then, that the large viscosity of the ternary electrolytes in glycerol is due to a summation of at least two effects; the small atomic volumes of barium, strontium, calcium, and cobalt, and possibly to some factor caused by solvation of the ions or molecules of the electrolytes, which, as stated above, would probably be greater with the salts of these metals than with salts of sodium, potassium, and ammonium.

Table 120 gives the corresponding viscosity data at 55°, 65°, and 75°. The same general relations seem to hold at the higher as at the lower temperatures. The temperature coefficients of fluidity at these higher temperatures are very similar to those of conductivity at the same temperatures.

From the data obtained, we are justified in concluding that curves representing change in conductivity and change in fluidity with rise in temperature are very similar to one another. In a word, conductivity seems to follow fluidity quite closely over the range of temperature from 25° to 75°.

The fact that glycerol has such a very large temperature coefficient of viscosity presents the possibility of throwing some light upon the relation between viscosity and reaction velocity. It has long been felt that the viscosity of the medium in which the reaction is taking place must be taken into consideration, and if the velocity of some reaction could be followed, using glycerol as a solvent, it is highly probable that interesting results would be obtained. Glycerol, being such an excellent solvent, seems well adapted to such work.

The viscosities and fluidities of solutions in the various mixtures of glycerol with the alcohols and with water are given in tables 121 to 123, inclusive. Measurements were made only with the tenth-normal solutions, since the viscosities of the more dilute solutions differ very slightly from that of the solvent in each case. Curves representing the change in fluidity with concentration of glycerol are given in fig. 80. These curves are, in general, strikingly analogous to the curves representing the conductivities in the same mixtures, though it is seen that the increase in fluidity is more rapid than the increase in conductivity. The viscosities of the solutions are in nearly every case greater than that of the pure solvent.

#### NEGATIVE VISCOSITY COEFFICIENTS.

One of the most interesting points brought out in this investigation is the fact that *certain salts have been found to lower the viscosity of glycerol*. The fact that certain electrolytes have the power to lower the viscosity of water has been known for some time. Jones and Veazey were the first to offer an apparently satisfactory explanation, the large atomic volumes of the metals whose salts produced such a change being the key to the phenomenon. The presence of elements with large atomic volumes, as has been stated, would decrease the amount of skin friction in a given volume of solution, and thus, in terms of the theory of Thorpe and Rodger, would decrease the viscosity. Jones and Veazey pointed out that only salts of potassium, rubidium, and caesium produce a decrease in the viscosity of water, and that these salts do so in a direct ratio to their respective atomic volumes. Schmidt had noted that the increase in viscosity of solutions in glycerol over that of the pure solvent was in an inverse ratio to the atomic volumes of the metals whose salts he studied; but in no case did he find a negative viscosity coefficient in pure glycerol.

The results showing negative viscosities in glycerol are given in table 124. From this table it can be seen that one-tenth gram-molecule of rubidium bromide lowers the viscosity of glycerol about 2 per cent, while one-half gram-molecule lowers the viscosity of the solvent over 8 per cent.



This lowering of the viscosity of glycerol by a salt of rubidium is analogous to the lowering of the viscosity of water produced by the same salt. The explanation of this phenomenon may be sought for in the theory of Jones and Veazey, *i. e.*, the large atomic volume of rubidium.

Ammonium bromide and ammonium iodide produce the same effect on the viscosity of glycerol, as is seen in table 124. It is clear that we can not speak of the atomic volume of ammonium, since we know of it neither in the "atomic" nor the "free" condition. It is, however, well known that ammonium is closely analogous chemically to potassium, caesium, and rubidium, and it is not surprising to find it exhibiting the same physical behavior, such as the effect on the viscosity of a solvent.

#### SUMMARY OF CONCLUSIONS DRAWN FROM THIS INVESTIGATION.

- (1) Glycerol forms mixtures with water, ethyl alcohol, and methyl alcohol, whose properties are not additive. This is in agreement with the work of Jones and Schmidt.
- (2) Curves representing fluidity and conductivity are very similar to one another over the range of temperature from 25° to 75°.
- (3) Salts which have the highest power of solvation show the greatest temperature coefficients of conductivity, and these are greater in the more dilute solutions.
- (4) In mixed solvents containing glycerol, with water, methyl and ethyl alcohols, the curves representing conductivity and fluidity are strikingly analogous.
- (5) The molecular conductivities of ternary electrolytes in glycerol at low dilutions are usually smaller than those of binary electrolytes under the same conditions, while at high dilutions the reverse is generally true.
- (6) While the majority of the salts studied increase the viscosity of glycerol, certain salts of rubidium and ammonium *lower the viscosity of glycerol*.
- (7) Some evidence for the existence of glycerolates has been given.

## WORK OF P. B. DAVIS.

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Prior to Jones and Veazey's investigation, Euler<sup>1</sup> had attempted to explain the lowering of the viscosity of a solvent by a dissolved substance, on the basis of the "electrostriction" of the solvent caused by the charge upon the ions of the solute as proposed by Drude and Nernst.<sup>2</sup> But Wagner and Mühlenbein<sup>3</sup> showed that Euler's explanation was not valid, since certain non-electrolytes in organic solvents also show negative viscosity, *e. g.*, cyanobenzol in ethyl alcohol.

The explanation offered by Jones and Veazey is based on their own observations and on the classical work of Thorpe and Rodger.<sup>4</sup> The latter have indicated that viscosity phenomena are in all probability dependent upon the frictional surfaces of the ultimate particles present in any liquid or solution. A review of the data obtained by Wagner<sup>5</sup> from his study of the viscosity of a number of inorganic salts in water will show that he found negative viscosity only in the case of caesium, rubidium, and potassium salts, and in some instances thallous salts. The first three metals occupy the maxima on the atomic volume curve of Lothar Meyer,<sup>6</sup> *i. e.*, they have the largest atomic volumes of all the elements. That some salts of potassium give positive viscosity is to be expected, since it has been shown that viscosity is an additive function of both the cation and the anion of the dissolved salt. In the case in question the one might tend to lower the viscosity of the solvent, the other to increase it, the final results depending upon whether the sum of these two opposing forces was positive or negative. Potassium has the smallest atomic volume of the three, and in many instances the positive viscosity effect of the anion would entirely overcome the negative effect of the cation.

In view of these facts, Jones and Veasey offered the apparently satisfactory explanation that "negative viscosity" is due to a lessening of the skin friction between the solvent and the molecules or ions of a solute, because of the large atomic volume of the cations as compared with the molecular aggregates of the solvent. This explanation follows directly from the work of Thorpe and Rodger.

W. Taylor<sup>7</sup> measured the viscosity of one, two, and three molar solutions of potassium chloride, bromide, and iodide in water at different temperatures, and noted that negative viscosity may pass over into positive viscosity with rise in temperature, and confirmed the view that viscosity depends upon the nature of both cation and anion. He noted also the negative viscosity effect of ammonium iodide when dissolved in water.

Reference should be made to the extensive work of Walden,<sup>8</sup> on the relations that exist between viscosity and conductivity at infinite dilutions. He finds that  $\mu_{\infty}\eta_{\infty} = C$  for more than thirty organic solvents. Exceptions have been noted to this relationship and these will be taken up later.

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<sup>1</sup>Zeit. phys. Chem., 25, 536 (1898).

<sup>2</sup>Ibid., 15, 79 (1894).

<sup>3</sup>Ibid., 46, 367 (1903).

<sup>4</sup>Phil. Trans., 185-A, 307 (1894).

<sup>5</sup>Zeit., phys. Chem., 15, 31 (1890).

<sup>6</sup>Ann. Chem. (Liebig), Suppl., 7, 354 (1870).

<sup>7</sup>Edin. Proc., 25, 228 (1904) and Edin. Trans., 45, 397 (1906).

<sup>8</sup>Zeit. phys. Chem., 78, 257 (1911).

## GLYCEROL AS A SOLVENT.

An examination of the literature bearing on this problem shows that only a little work had been done previous to that of Jones and Schmidt.

Cattaneo<sup>1</sup> measured the conductivity of several halides of the metals in glycerol, and noted that the values obtained were much smaller than the corresponding values in water or alcohol.

Schöttner<sup>2</sup> measured the viscosity of certain mixtures of glycerol and water. Arrhenius<sup>3</sup> studied the viscosity of mixtures of various organic substances with water, among them glycerol, and noted that the temperature coefficients of viscosity were greatest where the viscosity was greatest. Schall and Van Rijn<sup>4</sup> determined the relative viscosities of mixtures of glycerol with water and alcohol. Lemke<sup>5</sup> carried out an investigation on the conductivity and viscosity of water-glycerol mixtures at 25°, and was led to conclude that ionization, and hence electrical conductivity, is proportional to the viscosity of the solvent as well as to the association. He noted the periodic viscosity of sodium chloride in 9.8 per cent glycerol and water and a negative viscosity in water at certain dilutions. Getman<sup>6</sup> studied viscosity of potassium iodide in various organic solvents, including glycerol, and noted negative viscosity only in the case of the latter. This he attributed to the association of the solvent.

Jones and Schmidt<sup>7</sup> have studied the conductivity of lithium bromide, cobalt chloride, and potassium iodide in glycerol at 25°, 35°, and 45°, and in mixtures of glycerol with water, with ethyl alcohol, and with methyl alcohol at 25° and 35°. Measurements of viscosity were also made with the N/10 solution in the various solvents. They have shown that glycerol is an excellent solvent and in all probability a comparatively good dissociant, since it has a dielectric constant of 16.5 at 18° and an association factor of 1.8 at that temperature. From these data glycerol, according to the Thomson<sup>8</sup>-Nernst<sup>9</sup> and Dutoit and Aston<sup>10</sup> hypotheses, should have a dissociating power close to that of ethyl alcohol. The extremely low conductivity values obtained were attributed to the high viscosity of the solvent.

Schmidt noted that all the salts studied increased the viscosity of glycerol in N/10 solutions, but that potassium iodide lowered the viscosity of water, and of 25 and 50 per cent glycerol with water at 25° and 35°. He also showed that the effect of the several salts studied on the viscosity of glycerol was in inverse ratio to the atomic volumes of the cations, exactly analogous to the observations of Jones and Veazey in aqueous solutions. Schmidt also found glycerol to be an apparent exception to the observations of Walden<sup>11</sup> previously mentioned, that  $\mu_{\infty}\eta_{\infty} = C$ . Further exceptions in the case of water and glycerol have been noted by Walden from his own investigations.

The most extensive investigation of glycerol as a solvent has recently been carried out by Guy and Jones.<sup>12</sup> They took up the behavior of some twenty electrolytes in pure glycerol, and in binary mixtures of glycerol with ethyl alcohol, with methyl alcohol, and with water at intervals of 10° from 25° to 75° for the pure solvent and from 25° to 45° in mixed solvents. Conductivity measurements were made over a range of  $V = 10$  to  $V = 1,600$ , and viscosity measurements with the N/10 solutions.

<sup>1</sup>Rend. R. Acad. Lincei, [5], 2, II, 112 (1893).

<sup>2</sup>Wien. Ber., 77, II, 652 (1878).

<sup>3</sup>Zeit. phys. Chem., 1, 226 (1887).

<sup>4</sup>ibid., 23, 329 (1897).

<sup>5</sup>ibid., 52, 479 (1905).

<sup>6</sup>Journ. Amer. Chem. Soc., 30, 1077 (1908).

<sup>7</sup>Amer. Chem. Journ., 42, 37 (1909).

<sup>8</sup>Phil. Mag., 36, 320 (1898).

<sup>9</sup>Zeit. phys. Chem., 13, 531 (1894).

<sup>10</sup>Compt. Rend., 125, 240 (1897).

<sup>11</sup>Zeit. phys. Chem., 55, 246 ff. (1905), and 78, 267 (1911).

<sup>12</sup>Amer. Chem. Journ., 46, 131 (1911).

They found that molecular conductivities in glycerol are all extremely small, but show a regular increase with increased dilution and rise in temperature. Furthermore, a study of the temperature coefficients brought out the fact that in the case of those salts that have been shown to have large hydrating power in water, such as salts of barium, strontium, calcium, and cobalt, the relative increase was larger than with salts of sodium potassium and ammonium, which show little or no hydrating power in aqueous solutions. Here we have evidence of solvation in glycerol supporting that obtained by Jones and Strong<sup>1</sup> from spectroscopic methods.

In mixed solvents, Guy and Jones studied salts of potassium, sodium, ammonium, and strontium in various mixtures of glycerol with water and with ethyl and methyl alcohols. They found that conductivities in such mixtures do not follow the law of averages, but are always lower. This they explained by the facts established by Jones and Murray<sup>2</sup> and Jones and Lindsay,<sup>3</sup> that two highly associated solvents when mixed tend to break down the association each of the other, and hence their combined power of dissociating electrolytes is less than if there were no mutual lowering of their association, *i. e.*, if each solvent acted independently of the other.

From the viscosity data Guy and Jones have shown that the temperature coefficients of fluidity in pure glycerol are very large and nearly equal to those of conductivity. Also that the ternary electrolytes studied increased the viscosity of glycerol to a much greater extent than the binary electrolytes. This is attributed to the smaller atomic volumes of barium, strontium, calcium, and cobalt, and to the solvation of the molecules of the solute. In mixed solvents the curves representing conductivity and fluidity were found to be strikingly analogous.

Probably the most interesting point brought out by Guy and Jones was the large viscosity lowering observed in the case of certain salts in pure glycerol, *e. g.*, N/10 solutions of sodium nitrate, ammonium bromide, ammonium iodide, and rubidium bromide. The explanation of this phenomenon is derived from that of Jones and Veazey<sup>4</sup> for similar salts in water. This fact suggested the closer study of some of these salts over a wider range of concentration, the present investigation being a continuation of the work of Jones and Schmidt and of Guy and Jones.

Work on this problem was begun in collaboration with Wm. A. A. Reinhardt, of Baltimore, a graduate of Johns Hopkins University, whose untimely death proved a serious set-back to the carrying out of the investigation. We wish to pay tribute here to our friend and coworker as an earnest, sincere student, one who was rapidly coming to the front among the research students in this laboratory.

The conductivity data on ammonium iodide in mixed solvents obtained by Mr. Reinhardt are incorporated in this memoir.

#### EXPERIMENTAL.

##### APPARATUS.

The constant-temperature baths used in this investigation were of the form usually employed for such work in my laboratory. The thermostat for viscosity measurements was provided with glass windows, both in the front and rear, to facilitate the reading of the viscosimeters. Both baths were equipped with cooling coils in which the water was maintained at constant pressure. This facilitated temperature regu-

<sup>1</sup>Monographs Nos. 130 and 160, Carnegie Institution of Washington.  
<sup>2</sup>Amer. Chem. Journ., 30, 193 (1903).

<sup>3</sup>*Ibid.*, 28, 329 (1902).  
<sup>4</sup>*Loc. cit.*

lation below 35°. A closely fitting cover was provided for the conductivity bath for work above 35°, to prevent steaming and to maintain the air immediately above the cells at as near as possible the temperature of the water in the bath.

The temperature of the thermostats was maintained constant to within 0.02° by means of electrically controlled gas-regulators devised by Reid.<sup>1</sup> The thermometer used in the conductivity bath was of the usual 100° inclosed-scale type, graduated in 0.1°, and could be read to 0.02° with a hand lens. For work up to 45° the viscosity bath was provided with a 25° Beckmann thermometer graduated to 0.05° and with a certified Bender and Hobein thermometer for higher temperatures. All thermometers were first standardized against a certified Reichsanstalt instrument, and comparisons were frequently made during the course of the work.

The conductivity apparatus consisted of the usual Kohlrausch slide-wire bridge, resistance box, induction coil, and telephone receiver. This apparatus was made and standardized by Leeds and Northrup of Philadelphia, and in addition the resistances were compared with a rheostat which had been standardized by the Bureau of Standards, of Washington, D. C. The bridge wire was calibrated as directed by Jones<sup>2</sup> and found to be practically of uniform resistance throughout. Under favorable conditions separate readings with the same resistance agreed with one another to 0.5 mm., the nature of the solvent precluding closer agreements.

The conductivity cells used were of two types: Those of the ordinary plate type described by Jones and Bingham<sup>3</sup> had constants ranging from 40 to 339, and were used with the more concentrated solutions. For the N/10 to N/1600 solutions, five cells of the type previously described by Jones and Schmidt<sup>4</sup> and by Jones and Kreider<sup>5</sup> were used. Their constants ranged from 2.35 to 4.36, and because of this they were well adapted to the measurement of high resistances.

Cell constants were determined with a fiftieth-normal potassium chloride solution as a basis, this being diluted to N/500 and N/2000 for the low constant cells. Checks were made at regular intervals, and showed only slight variations in the cell constants, especially in the case of the cells with concentric cylindrical electrodes.

The molecular conductivity of the fiftieth-normal solution was taken as 129.7 reciprocal Siemens units, at 25°. That of the more dilute solutions was determined by direct measurements.

Viscosity measurements were made with the Ostwald viscosimeter<sup>6</sup> as modified by Jones and Veazey,<sup>7</sup> the sizes of the capillaries being adapted to the solutions for which they were employed. The viscosimeters were calibrated as described by Jones and Schmidt,<sup>8</sup> the time of flow for water in the instruments used for glycerol being derived from the formula

$$t_W''' = \frac{t_W' \cdot t_A'' \cdot t_B'''}{t_A' \cdot t_B''}$$

where  $t_W'$  is the time of flow of water in the water viscosimeter,  $t_A'$  the time for a slightly more viscous solution in the water viscosimeter,  $t_A''$ ,  $t_B''$  and  $t_B'''$  the times of flow of the solutions A and B of intermediate viscosities between water and glycerol in an intermediate viscosimeter and in the instrument for glycerol;  $t_W'''$  the derived time

<sup>1</sup>Amer. Chem. Journ., 41, 148 (1909).

<sup>2</sup>Freezing Point, Boiling Point and Conductivity Methods.

<sup>3</sup>Amer. Chem. Journ., 34, 481 (1906).

<sup>4</sup>*Ibid.*, 42, 39 (1909).

<sup>5</sup>*Ibid.*, 45, 282 (1911).

<sup>6</sup>Oswald-Luther: *Physiko-chemische Mess.*, 2d ed. (1910).

p. 232.

<sup>7</sup>Zeit. phys. Chem., 61, 641 (1908).

<sup>8</sup>*Loc. cit.*

of flow in the glycerol viscosimeter. The viscosimeters were filled by means of carefully calibrated pipettes with such a volume of liquid as was required to fill them from the middle of the upper to the middle of the lower bulb. With such an arrangement, according to Appleby<sup>1</sup> the alteration in hydrostatic pressure due to small variations in the volume of the liquid is a minimum.

On account of the steaming of the viscosity thermostat at high temperatures, the viscosimeters after filling were provided with a simple apparatus designed to exclude dust and moisture, and to eliminate the danger of obstructing the free passage of air from one arm of the viscosimeter to the other during the flow of the liquid through the capillary. This consisted of two T-shaped guard tubes each provided with a small bulb in the long arm. These bulbs were filled with cotton-wool to filter out dust particles. One end of the cross-arm of a guard tube was connected to each arm of the viscosimeter, and the opposite ends joined by a short piece of rubber tubing. The liquid was drawn up in the capillary arm of the viscosimeter by compressing the rubber tube and attaching the bulb arm of the guard tube on that side to an aspirator. The air entering through the guard tube on the opposite (reservoir) arm is thoroughly dried by passing over calcium chloride and freed from dust by the cotton wool mentioned above. When the liquid has risen to a point slightly above the upper mark on the viscosimeter, the compression on the rubber tube is released and the air pressure immediately equalizes itself on both sides of the viscosimeter. By this arrangement no air from the outside enters during the actual flow of the liquid through the capillary.

Viscosimeters, while being read, were supported in the bath by means of special clamps with cork-lined jaws, attached to a heavy stand which was carefully leveled.

Specific-gravity determinations were made by means of the Ostwald pycnometer as modified for liquids with large expansion by Jones and Veazey.

All measuring flasks and pipettes were carefully calibrated either by direct weighing or by the method of Morse and Blalock<sup>2</sup> to hold aliquot parts of the true liter at 20°, and solutions were brought to within 0.1° of this temperature before being diluted to the mark.

#### SOLUTIONS.

Because of a limited supply of salts at hand all solutions were made up at 20° and a temperature correction made for temperatures above 25°. The expansion coefficient for glycerol was taken as 0.00049 and was determined from specific-gravity measurements in the viscosity work.

Solutions of the N/0.75, N/2, N/4, and N/10 were made by direct weighing of the anhydrous salt, which had been previously dried for some time in an air-bath at 130° to 135°. From the N/10 solution the N/50 and N/100 solutions were made by dilution. These in turn served as mother-solutions for the N/200 and N/400, from which the N/800 and N/1600 solutions were made in a similar manner. The latter was made by diluting the N/400 solution four times.

Because of the hygroscopic nature of the solvent and the difficulty in obtaining proper drainage of burettes containing it, measuring flasks were used exclusively in the dilution of solutions in glycerol. In every case the proper measuring flask was filled with the mother-solution, set in a thermostat at 20°, warmed in an air-bath to

<sup>1</sup>Journ. Chem. Soc., 972, 2000 (1910).

<sup>2</sup>Amer. Chem. Journ., 16, 479 (1904).

70° to 80°, drained as quickly as possible into the receiving flask, then washed out at least three times with the warmed solvent. The flask containing the more dilute solution was then filled up nearly to the neck with the solvent, warmed and shaken thoroughly without wetting the neck, then filled to a point slightly above the mark, and finally diluted after cooling to 20° in a thermostat. Final warming in the air-bath and thorough shaking completed the operation. The flasks used were of Jena normal glass, eliminating as far as possible the danger of the action of the solvent on the glass. Some time was allowed before the final dilution to the mark to permit the glass to contract properly after the unavoidable heating during the process of dilution.

On account of the extremely high resistance offered by glycerol solutions conductivity measurements were not made at dilutions greater than N/1600. Even at that dilution considerable difficulty was experienced in obtaining concordant readings. As an example it might be well to note that N/1600 solutions in glycerol in a cell with a constant as low as 2.3 required a balancing resistance of from 8,000 to 10,000 ohms, while pure glycerol in the same cell required 20,000 to 22,000 ohms.

Conductivity and viscosity measurements in pure glycerol were made at intervals of ten degrees from 20° to 75°, and in glycerol-water mixtures at 25°, 35°, and 45°. Viscosity measurements were not made at a greater dilution than N/10, since at lower concentration  $\eta$  approaches  $\eta_{\infty}$  too closely to be accurately differentiated.

#### SOLVENTS.

*Glycerol.*—The glycerol used was from a new lot of Kahlbaum's "Doppelt-Dist. 1.26" and had a mean specific conductivity of about  $0.6 \times 10^{-7}$  at 25°, and a mean specific gravity of 1.257 at the same temperature. No attempt was made to redistill it, since Schmidt had already shown that redistillation did not appreciably lower the conductivity.

*Water.*—The water was purified by the method of Jones and Mackay<sup>1</sup> with the improvement as mentioned by Schmidt and had a mean specific conductivity of  $1.5 \times 10^{-7}$  at 25°.

#### SALTS.

The rubidium and ammonium salts used in this work were from Kahlbaum's best products. These were recrystallized two or three times from conductivity water and carefully dried each time at 130° to 135° before weighing. In addition the rubidium salts were examined spectroscopically and showed the presence of only traces of sodium and no potassium. The ammonium iodide was pure white after drying, and solutions of it in glycerol were only slightly tinted after standing for some time.

#### PROCEDURE.

Conductivity data were calculated in the usual way.

Viscosity measurements were calculated from the formula

$$\frac{\eta}{\eta_0} = \frac{St}{S_0 t_0}$$

in which  $\eta$  is the viscosity coefficient for the liquid in question,  $\eta_0$  the absolute viscosity of water,  $S$  the specific gravity of the liquid at the given temperature,  $t$  the time of flow of the same,  $S_0$  and  $t_0$  the density and time of flow of water at the same temperature.

<sup>1</sup>Amer. Chem. Journ., 17, 83 (1895).

Fluidity was calculated from the formula  $\phi = \frac{1}{\eta}$ , where  $\phi$  represents the fluidity.

The absolute viscosities of water  $\eta_0$  as given by Thorpe and Rodger are:

25°.....	0.00891	55°.....	0.005055
35°.....	0.00720	65°.....	0.004355
45°.....	0.00597	75°.....	0.003795

## TEMPERATURE COEFFICIENTS.

The temperature coefficients in conductivity units represent simply the actual increase in conductivity per degree rise in temperature.

Per cent temperature coefficients, both of conductivity and fluidity, were calculated from the formula

$$\text{Temp. coeff. of } (\mu, \phi) = \frac{1}{(\mu, \phi)_{25^\circ}} \cdot \frac{(\mu, \phi)_{35^\circ} - (\mu, \phi)_{25^\circ}}{10}$$

An attempt was made to obtain conductivity and viscosity data on the sulphate of rubidium, but it was not possible to obtain a solution of higher concentration than N/200.

It was originally intended to carry on a parallel investigation with caesium salts, but we have been unable thus far to secure sufficient quantities for the work.

TABLE 126.—*Molecular Conductivity of Ammonium Iodide in Glycerol at 25°, 35°, 45°, 55°, 65°, and 75°, together with Temperature Coefficients in Per Cent and in Conductivity Units.*

V	Molecular conductivities.					
	$\mu, 25^\circ$	$\mu, 35^\circ$	$\mu, 45^\circ$	$\mu, 55^\circ$	$\mu, 65^\circ$	$\mu, 75^\circ$
1	0.389	0.770	1.385	2.304	3.602	5.260
1.3	0.371	0.746	1.361	2.268	3.540	5.189
2	0.348	0.717	1.312	2.140	3.404	5.072
4	0.326	0.665	1.224	2.069	3.266	4.858
10	0.342	0.700	1.321	2.210	3.506	5.278
50	0.359	0.740	1.373	2.331	3.707	5.534
100	0.369	0.764	1.414	2.424	3.843	5.772
200	0.365	0.760	1.396	2.386	3.805	5.606
400	0.371	0.753	1.401	2.410	3.819	5.749
800	0.404	0.777	1.441	2.485	4.010	5.950
1,600	0.413	0.811	1.457	2.528	4.130	6.100

V	Temperature coefficients.									
	Per cent.					Conductivity units.				
	25 to 35°	35 to 45°	45 to 55°	55 to 65°	65 to 75°	25 to 35°	35 to 45°	45 to 55°	55 to 65°	65 to 75°
1	0.0979	0.0799	0.0663	0.0563	0.0460	0.0381	0.0615	0.0919	0.1298	0.1658
1.3	0.1012	0.0824	0.0666	0.0561	0.0466	0.0375	0.0615	0.0907	0.1272	0.1649
2	0.1060	0.0830	0.0631	0.0591	0.0490	0.0369	0.0595	0.0828	0.1264	0.1668
4	0.1040	0.0841	0.0690	0.0578	0.0487	0.0339	0.0559	0.0845	0.1197	0.1592
10	0.1047	0.0887	0.0673	0.0586	0.0505	0.0358	0.0621	0.0889	0.1296	0.1772
50	0.1061	0.0855	0.0698	0.0590	0.0493	0.0381	0.0633	0.0958	0.1376	0.1827
100	0.1070	0.0851	0.0714	0.0585	0.0476	0.0395	0.0650	0.1010	0.1419	0.1829
200	0.1082	0.0837	0.0709	0.0590	0.0473	0.0395	0.0636	0.0990	0.1419	0.1801
400	0.1030	0.0860	0.0720	0.0585	0.0505	0.0382	0.0648	0.1009	0.1409	0.1930
800	0.0923	0.0854	0.0724	0.0614	0.0484	0.0373	0.0664	0.1044	0.1525	0.1940
1,600	0.0964	0.0797	0.0735	0.0634	0.0477	0.0398	0.0646	0.1071	0.1602	0.1970



TABLE 127.—*Molecular Conductivity of Rubidium Chloride in Glycerol at 25°, 35°, 45°, 55°, 65°, and 75°, together with Temperature Coefficients in Per Cent and in Conductivity Units.*

V	Molecular conductivities.					
	$\mu_{25^\circ}$	$\mu_{35^\circ}$	$\mu_{45^\circ}$	$\mu_{55^\circ}$	$\mu_{65^\circ}$	$\mu_{75^\circ}$
1	0.374	0.738	1.320	2.205	3.400	4.994
1.3	0.371	0.740	1.337	2.215	3.421	5.014
2	0.386	0.767	1.371	2.307	3.570	5.272
4	0.376	0.771	1.390	2.310	3.585	5.382
10	0.380	0.771	1.410	2.386	3.749	5.684
50	0.401	0.819	1.502	2.561	4.003	6.041
100	0.420	0.848	1.563	2.649	4.180	6.343
200	0.428	0.860	1.588	2.720	4.282	6.408
400	0.432	0.887	1.633	2.784	4.408	6.542
800	0.444	0.874	1.625	2.774	4.358	6.532
1,600	0.448	0.892	1.643	2.831	4.462	6.574

V	Temperature coefficients.									
	Per cent.					Conductivity units.				
	25 to 35°	35 to 45°	45 to 55°	55 to 65°	65 to 75°	25 to 35°	35 to 45°	45 to 55°	55 to 65°	65 to 75°
1	0.0973	0.0789	0.0670	0.0542	0.0469	0.0364	0.0582	0.0885	0.1195	0.1504
1.3	0.0995	0.0807	0.0657	0.0544	0.0466	0.0369	0.0597	0.0878	0.1206	0.1593
2	0.0987	0.0812	0.0677	0.0547	0.0477	0.0381	0.0623	0.0936	0.1263	0.1702
4	0.1050	0.0784	0.0662	0.0553	0.0501	0.0395	0.0604	0.0920	0.1275	0.1797
10	0.1029	0.0829	0.0692	0.0571	0.0516	0.0391	0.0639	0.0976	0.1363	0.1935
50	0.1042	0.0834	0.0705	0.0563	0.0509	0.0418	0.0683	0.1059	0.1442	0.2038
100	0.1019	0.0843	0.0695	0.0578	0.0517	0.0428	0.0715	0.1086	0.1531	0.2163
200	0.1009	0.0846	0.0713	0.0574	0.0496	0.0432	0.0728	0.1132	0.1562	0.2126
400	0.1053	0.0841	0.0705	0.0547	0.0484	0.0455	0.0746	0.1151	0.1524	0.2134
800	0.0970	0.0859	0.0707	0.0571	0.0498	0.0430	0.0751	0.1149	0.1584	0.2174
1,600	0.0991	0.0842	0.0723	0.0576	0.0473	0.0444	0.0751	0.1188	0.1631	0.2112

TABLE 128.—*Molecular Conductivity of Rubidium Bromide in Glycerol at 25°, 35°, 45°, 55°, 65°, and 75°, together with Temperature Coefficients in Per Cent and in Conductivity Units.*

V	Molecular conductivities.					
	$\mu_{25^\circ}$	$\mu_{35^\circ}$	$\mu_{45^\circ}$	$\mu_{55^\circ}$	$\mu_{65^\circ}$	$\mu_{75^\circ}$
1	0.368	0.717	1.273	2.143	3.056	4.595
1.3	0.360	0.716	1.311	2.198	3.424	4.604
4	0.363	0.732	1.339	2.217	3.489	5.120
10	0.369	0.752	1.385	2.324	3.676	5.483
50	0.379	0.785	1.456	2.473	3.876	5.763
100	0.409	0.835	1.483	2.623	4.153	6.236
200	0.427	0.855	1.592	2.698	4.291	6.477
400	0.451	0.879	1.627	2.711	4.348	6.592
800	0.470	0.893	1.633	2.724	4.401	6.666
1,600	0.480	0.932	1.700	2.722	4.499	6.855

V	Temperature coefficients.									
	Per cent.					Conductivity units.				
	25 to 35°	35 to 45°	45 to 55°	55 to 65°	65 to 75°	25 to 35°	35 to 45°	45 to 55°	55 to 65°	65 to 75°
1	0.0948	0.0775	0.0683	0.0426	0.0504	0.0349	0.0556	0.0870	0.0913	0.1539
1.3	0.0989	0.0831	0.0677	0.0558	0.0345	0.0356	0.0595	0.0887	0.1226	0.1180
4	0.1016	0.0828	0.0656	0.0569	0.0318	0.0369	0.0607	0.0878	0.1262	0.1631
10	0.1037	0.0842	0.0678	0.0580	0.0492	0.0383	0.0633	0.0939	0.1352	0.1807
50	0.1071	0.0855	0.0698	0.0567	0.0487	0.0406	0.0671	0.1017	0.1402	0.1887
100	0.1057	0.0776	0.0769	0.0583	0.0501	0.0429	0.0648	0.1140	0.1530	0.2083
200	0.1036	0.0862	0.0693	0.0590	0.0509	0.0435	0.0737	0.1104	0.1593	0.2186
400	0.1011	0.0851	0.0650	0.0604	0.0516	0.0442	0.0748	0.1058	0.1637	0.2244
800	0.1020	0.0829	0.0668	0.0616	0.0515	0.0451	0.0740	0.1091	0.1677	0.2265
1,600	0.1198	0.0824	0.0601	0.0653	0.0524	0.0508	0.0768	0.1022	0.1777	0.2356

TABLE 129.—*Molecular Conductivity of Rubidium Iodide in Glycerol at 25°, 35°, 45°, 55°, 65°, and 75°, together with Temperature Coefficients in Per Cent and in Conductivity Units.*

V	Molecular conductivities.					
	$\mu_9$ 25°	$\mu_9$ 35°	$\mu_9$ 45°	$\mu_9$ 55°	$\mu_9$ 65°	$\mu_9$ 75°
1	0.355	0.704	1.275	2.111	3.229	4.771
1.3	0.342	0.688	1.252	2.100	3.286	4.812
2	0.334	0.680	1.236	2.089	3.278	4.829
4	0.321	0.649	1.212	2.034	3.197	4.703
10	0.323	0.657	1.213	2.007	3.103	4.667
50	0.345	0.703	1.330	2.256	3.575	5.408
100	0.356	0.721	1.361	2.320	3.687	5.466
200	0.363	0.745	1.373	2.360	3.861	5.743
400	0.368	0.751	1.391	2.408	3.937	5.832
800	0.370	0.781	1.380	2.405	3.941	5.756
1,600	0.373	0.805	1.389	2.395	4.150	5.809

V	Temperature coefficients.									
	Per cent.					Conductivity units.				
	25 to 35°	35 to 45°	45 to 55°	55 to 65°	65 to 75°	25 to 35°	35 to 45°	45 to 55°	55 to 65°	65 to 75°
1	0.0983	0.0810	0.0656	0.0530	0.0474	0.0349	0.0571	0.0836	0.1118	0.1542
1.3	0.1012	0.0819	0.0677	0.0565	0.0464	0.0346	0.0564	0.0848	0.1186	0.1526
2	0.1036	0.0818	0.0690	0.0569	0.0473	0.0346	0.0556	0.0853	0.1189	0.1551
4	0.1022	0.0867	0.0678	0.0572	0.0471	0.0328	0.0563	0.0822	0.1163	0.1506
10	0.1034	0.0846	0.0674	0.0546	0.0499	0.0334	0.0556	0.0794	0.1096	0.1564
50	0.1038	0.0892	0.0696	0.0584	0.0541	0.0358	0.0627	0.0926	0.1318	0.1833
100	0.1025	0.0888	0.0705	0.0588	0.0455	0.0365	0.0640	0.0960	0.1366	0.1779
200	0.1052	0.0844	0.0719	0.0638	0.0487	0.0382	0.0628	0.0987	0.1501	0.1882
400	0.1041	0.0857	0.0731	0.0635	0.0481	0.0383	0.0644	0.1017	0.1529	0.1895
800	0.1110	0.0767	0.0742	0.0628	0.0461	0.0411	0.0599	0.1025	0.1536	0.1815
1,600	0.1159	0.0725	0.0724	0.0732	0.0402	0.0432	0.0584	0.1006	0.1755	0.1659

TABLE 130.—*Molecular Conductivity of Rubidium Nitrate in Glycerol at 25°, 35°, 45°, 55°, 65°, and 75°, together with Temperature Coefficients in Per Cent and in Conductivity Units.*

V	Molecular conductivities.					
	$\mu_9$ 25°	$\mu_9$ 35°	$\mu_9$ 45°	$\mu_9$ 55°	$\mu_9$ 65°	$\mu_9$ 75°
2	0.299	0.625	1.093	1.930	3.005	4.435
4	0.294	0.611	1.127	1.913	2.979	4.392
10	0.325	0.666	1.228	2.088	3.272	4.866
50	0.366	0.742	1.384	2.350	3.712	5.570
100	0.386	0.793	1.450	2.481	3.917	5.894
200	0.388	0.793	1.490	2.495	4.000	5.960
400	0.407	0.801	1.471	2.487	3.932	5.862
800	0.417	0.873	1.550	2.605	4.161	6.174

V	Temperature coefficients.									
	Per cent.					Conductivity units.				
	25 to 35°	35 to 45°	45 to 55°	55 to 65°	65 to 75°	25 to 35°	35 to 45°	45 to 55°	55 to 65°	65 to 75°
2	0.1090	0.0749	0.0763	0.0557	0.0475	0.0326	0.0468	0.0837	0.1075	0.1430
4	0.1078	0.0844	0.0698	0.0557	0.0474	0.0317	0.0516	0.0786	0.1066	0.1413
10	0.1046	0.0844	0.0700	0.0568	0.0487	0.0341	0.0562	0.0860	0.1184	0.1594
50	0.1027	0.0865	0.0699	0.0579	0.0505	0.0376	0.0642	0.0966	0.1362	0.1858
100	0.1051	0.0829	0.0710	0.0579	0.0505	0.0407	0.0657	0.1031	0.1436	0.1977
200	0.1044	0.0879	0.0674	0.0602	0.0491	0.0405	0.0697	0.1005	0.1505	0.1963
400	0.0968	0.0836	0.0690	0.0581	0.0491	0.0394	0.0670	0.1016	0.1445	0.1930
800	0.1096	0.0776	0.0680	0.0597	0.0483	0.0456	0.0677	0.1055	0.1556	0.2013

TABLE 131.—*Molecular Conductivity of Ammonium Iodide in a Mixture of 75 Per Cent Glycerol with Water at 25°, 35°, and 45°, together with Temperature Coefficients in Per Cent and in Conductivity Units.*

V	Molecular conductivities.			Temperature coefficients.			
				Per cent.		Conductivity units.	
	$\mu_9$ 25°	$\mu_9$ 35°	$\mu_9$ 45°	25 to 35°	35 to 45°	25 to 35°	35 to 45°
1	5.48	8.24	11.61	0.0504	0.0409	0.276	0.337
1.3	5.39	8.11	11.53	0.0505	0.0422	0.292	0.342
2	5.24	8.00	11.50	0.0527	0.0437	0.276	0.350
4	5.18	7.99	11.47	0.0542	0.0435	0.281	0.348
10	5.26	8.16	11.75	0.0551	0.0440	0.290	0.359
50	5.56	8.64	12.56	0.0572	0.0454	0.318	0.392
100	5.71	8.89	12.94	0.0557	0.0456	0.318	0.405
200	5.81	9.05	13.19	0.0558	0.0457	0.324	0.414
400	5.76	8.99	13.18	0.0561	0.0466	0.323	0.419
800	6.06	9.44	13.74	0.0560	0.0456	0.339	0.430
1,600	6.03	9.39	13.73	0.0557	0.0462	0.336	0.434

TABLE 132.—*Molecular Conductivity of Ammonium Iodide in a Mixture of 50 Per Cent Glycerol with Water at 25°, 35°, and 45°, together with Temperature Coefficients in Per Cent and in Conductivity Units.*

V	Molecular conductivities.			Temperature coefficients.			
				Per cent.		Conductivity units.	
	$\mu_9$ 25°	$\mu_9$ 35°	$\mu_9$ 45°	25 to 35°	35 to 45°	25 to 35°	35 to 45°
1	22.38	29.40	37.24	0.0314	0.0267	0.702	0.784
1.3	22.19	29.36	37.25	0.0323	0.0269	0.717	0.789
2	22.12	29.51	37.55	0.0334	0.0272	0.739	0.804
10	23.15	31.27	40.34	0.0351	0.0290	0.812	0.907
50	24.69	33.40	43.16	0.0353	0.0292	0.871	0.976
100	25.52	34.54	44.83	0.0353	0.0301	0.902	1.029
200	25.49	34.66	45.18	0.0360	0.0303	0.917	1.052
400	25.68	35.20	45.30	0.0371	0.0287	0.952	1.010
800	26.29	35.87	46.18	0.0364	0.0287	0.958	1.031
1,600	26.62	36.21	47.00	0.0360	0.0298	0.959	1.079

TABLE 133.—*Molecular Conductivity of Ammonium Iodide in a Mixture of 25 Per Cent Glycerol with Water at 25°, 35°, and 45°, together with Temperature Coefficients in Per Cent and in Conductivity Units.*

V	Molecular conductivities.			Temperature coefficients.			
				Per cent.		Conductivity units.	
	$\mu_9$ 25°	$\mu_9$ 35°	$\mu_9$ 45°	25 to 35°	35 to 45°	25 to 35°	35 to 45°
10	61.58	76.71	92.62	0.0246	0.0207	1.513	1.591
50	64.32	80.30	98.25	0.0248	0.0223	1.598	1.795
100	66.69	82.86	101.50	0.0242	0.0225	1.617	1.864
200	68.54	85.87	104.39	0.0256	0.0201	1.733	1.852
400	68.12	85.07	104.17	0.0249	0.0224	1.695	1.910
800	69.21	87.26	105.92	0.0261	0.0214	1.805	1.866
1,600	69.68	88.47	106.85	0.0269	0.0208	1.879	1.838

TABLE 134.—*Molecular Conductivity of Ammonium Iodide in Water at 25°, 35°, and 45°, together with Temperature Coefficients in Per Cent and in Conductivity Units.*

V	Molecular conductivities.			Temperature coefficients.			
				Per cent.		Conductivity units.	
	$\mu_9$ 25°	$\mu_9$ 35°	$\mu_9$ 45°	25 to 35°	35 to 45°	25 to 35°	35 to 45°
1.3	100.7	114.1	130.4	0.0133	0.0143	1.34	1.63
2	102.5	125.3	147.5	0.0222	0.0178	2.28	2.22
4	105.3	125.8	151.3	0.0195	0.0202	2.05	2.55
10	121.3	148.6	172.6	0.0225	0.0161	2.73	2.40
50	135.2	160.5	186.3	0.0187	0.0160	2.53	2.58
100	136.3	161.3	190.8	0.0184	0.0182	2.60	2.95
200	139.0	168.5	197.7	0.0212	0.0173	2.95	2.92
400	143.1	171.2	202.9	0.0196	0.0185	2.81	3.17
800	151.1	182.0	215.1	0.0204	0.0176	3.09	3.21
1,600	154.7	184.6	218.4	0.0193	0.0183	2.99	3.38

TABLE 135.—*Molecular Conductivity of Rubidium Bromide in a Mixture of 75 Per Cent Glycerol with Water at 25°, 35°, and 45°, together with Temperature Coefficients in Per Cent and in Conductivity Units.*

V	Molecular conductivities.			Temperature coefficients.			
				Per cent.		Conductivity units.	
	$\mu_9$ 25°	$\mu_9$ 35°	$\mu_9$ 45°	25 to 35°	35 to 45°	25 to 35°	35 to 45°
1	5.33	7.81	10.87	0.0465	0.0392	0.248	0.306
1.3	5.31	7.94	11.07	0.0495	0.0394	0.263	0.313
2	5.39	8.05	11.57	0.0494	0.0437	0.266	0.352
4	5.43	8.28	11.79	0.0525	0.0424	0.285	0.351
10	5.67	8.63	12.31	0.0522	0.0426	0.296	0.368
50	6.15	9.31	13.46	0.0514	0.0446	0.316	0.415
100	6.27	9.67	13.86	0.0542	0.0433	0.340	0.419
200	6.35	9.79	14.11	0.0542	0.0441	0.344	0.432
400	6.41	9.87	14.28	0.0540	0.0448	0.346	0.441
800	6.52	10.03	14.45	0.0538	0.0441	0.351	0.442
1,600	6.52	10.07	14.51	0.0544	0.0441	0.355	0.444

TABLE 136.—*Molecular Conductivity of Rubidium Bromide in a Mixture of 50 Per Cent Glycerol with Water at 25°, 35°, and 45°, together with Temperature Coefficients in Per Cent and in Conductivity Units.*

V	Molecular conductivities.			Temperature coefficients.			
				Per cent.		Conductivity units.	
	$\mu_9$ 25°	$\mu_9$ 35°	$\mu_9$ 45°	25 to 35°	35 to 45°	25 to 35°	35 to 45°
1	21.65	27.98	35.27	0.0292	0.0261	0.633	0.729
1.3	21.38	28.33	36.37	0.0325	0.0284	0.695	0.804
2	22.31	28.90	36.75	0.0295	0.0280	0.659	0.785
4	23.33	30.84	39.31	0.0321	0.0281	0.751	0.847
10	24.51	32.73	41.85	0.0335	0.0279	0.822	0.912
50	26.25	34.85	44.92	0.0328	0.0289	0.860	1.007
100	26.87	36.02	46.72	0.0340	0.0297	0.915	1.070
200	27.54	37.01	48.17	0.0344	0.0301	0.947	1.116
400	27.97	37.47	48.39	0.0340	0.0292	0.950	1.092
800	28.47	38.35	49.60	0.0347	0.0293	0.988	1.125
1,600	28.39	38.33	49.48	0.0350	0.0291	0.994	1.115

TABLE 137.—*Molecular Conductivity of Rubidium Bromide in a Mixture of 25 Per Cent Glycerol with Water at 25°, 35°, and 45°, together with Temperature Coefficients in Per Cent and in Conductivity Units.*

V	Molecular conductivities.			Temperature coefficients.			
				Per cent.		Conductivity units.	
	$\mu_{25^\circ}$	$\mu_{35^\circ}$	$\mu_{45^\circ}$	25 to 35°	35 to 45°	25 to 35°	35 to 45°
2	51.79	65.77	79.87	0.0270	0.0214	1.396	1.410
4	54.23	67.23	81.80	0.0240	0.0217	1.300	1.457
10	62.88	76.85	93.67	0.0222	0.0219	1.397	1.682
50	69.27	84.84	103.77	0.0225	0.0223	1.557	1.893
100	69.44	86.22	105.46	0.0239	0.0223	1.678	1.924
200	71.39	89.09	108.43	0.0248	0.0217	1.770	1.934
400	73.40	91.15	111.22	0.0242	0.0220	1.775	2.007
800	74.16	92.10	111.81	0.0242	0.0214	1.794	1.971
1,600	82.85	101.59	123.19	0.0226	0.0213	1.874	2.160

TABLE 138.—*Molecular Conductivity of Rubidium Bromide in Water at 25°, 35°, and 45°, together with Temperature Coefficients in Per Cent and in Conductivity Units.*

V	Molecular conductivities.			Temperature coefficients.			
				Per cent.		Conductivity units.	
	$\mu_{25^\circ}$	$\mu_{35^\circ}$	$\mu_{45^\circ}$	25 to 35°	35 to 45°	25 to 35°	35 to 45°
2	96.3	119.8	137.4	0.0243	0.0147	2.35	1.76
4	107.8	132.1	153.3	0.0226	0.0160	2.43	2.12
10	121.8	143.8	165.8	0.0181	0.0153	2.20	2.20
50	137.2	163.0	189.3	0.0188	0.0162	2.58	2.63
100	142.2	167.2	195.4	0.0176	0.0169	2.50	2.82
200	143.3	170.1	199.9	0.0187	0.0175	2.68	2.98
400	148.4	174.9	202.2	0.0178	0.0156	2.65	2.73
800	152.8	179.1	208.3	0.0172	0.0163	2.63	2.92
1,600	151.8	179.9	211.7	0.0185	0.0177	2.81	3.18

TABLE 139.—*Comparison of Temperature Coefficients of Ammonium Iodide and Rubidium Bromide from 25° to 35° in Mixtures of Glycerol and Water.*

V	Ammonium iodide.					Rubidium bromide.				
	100 p. ct.	75 p. ct.	50 p. ct.	25 p. ct.	0 p. ct.	100 p. ct.	75 p. ct.	50 p. ct.	25 p. ct.	0 p. ct.
10	0.1047	0.0551	0.0351	0.0246	0.0225	0.1037	0.0522	0.0335	0.0222	0.0181
50	0.1061	0.0572	0.0353	0.0248	0.0187	0.1071	0.0514	0.0328	0.0225	0.0188
100	0.1070	0.0557	0.0353	0.0242	0.0184	0.1057	0.0542	0.0340	0.0239	0.0176
200	0.1082	0.0558	0.0360	0.0256	0.0212	0.1036	0.0542	0.0344	0.0248	0.0187
400	0.1030	0.0561	0.0371	0.0249	0.0196	0.1011	0.0540	0.0340	0.0242	0.0178
800	0.0923	0.0560	0.0364	0.0261	0.0204	0.1020	0.0538	0.0347	0.0242	0.0172
1,600	0.0964	0.0557	0.0360	0.0269	0.0193	0.1198	0.0544	0.0350	0.0226	0.0185

TABLE 140.—*Viscosity and Fluidity of Various Compounds in Glycerol, with Temperature Coefficients of Fluidity.*

	Mol. conc.	$\eta$ 25°	$\eta$ 35°	$\eta$ 45°	$\eta$ 55°	$\eta$ 65°	$\eta$ 75°	$\phi$ 25°	$\phi$ 35°	$\phi$ 45°	$\phi$ 55°	$\phi$ 65°	$\phi$ 75°	Temperature coefficients.				
														25 to 35°	35 to 45°	45 to 55°	55 to 65°	65 to 75°
Ammonium iodide in glycerol.....	1.00	4.399	2.063	1.071	0.59270	0.36230	0.22640	0.22730	0.48470	0.93351	0.887	2.760	4.416	0.113	0.093	0.081	0.063	0.060
	0.75	4.769	2.219	1.139	0.62150	0.37720	0.23440	0.20970	0.45060	0.87821	0.909	2.651	4.266	0.115	0.095	0.083	0.065	0.061
	0.50	5.119	2.355	1.205	0.65400	0.38500	0.24240	0.19330	0.42460	0.82951	0.929	2.597	4.126	0.117	0.095	0.084	0.070	0.059
	0.25	5.498	2.511	1.275	0.68070	0.39630	0.25160	0.18190	0.39820	0.78411	0.949	2.523	3.975	0.119	0.096	0.087	0.072	0.058
	0.10	5.766	2.623	1.325	0.70900	0.40280	0.25770	0.17340	0.38120	0.75451	0.975	2.452	3.890	0.120	0.098	0.087	0.075	0.056
Solv.	5.828	2.648	1.332	0.71000	0.40760	0.25580	0.17160	0.37760	0.75001	0.968	2.453	3.909		0.099	0.087	0.074	0.059	
Rubidium chloride in glycerol.....	1.00	5.240	2.439	1.264	0.68670	0.41770	0.25950	0.19080	0.40980	0.79101	0.956	2.394	3.854	0.115	0.095	0.084	0.064	0.061
	0.75	5.351	2.500	1.282	0.69220	0.41950	0.25890	0.18990	0.40000	0.78011	0.955	2.384	3.862	0.114	0.095	0.085	0.065	0.062
	0.50	5.542	2.547	1.307	0.70430	0.43110	0.26040	0.18040	0.32960	0.76511	0.920	2.307	3.840	0.118	0.095	0.086	0.062	0.069
	0.25	5.711	2.616	1.328	0.71300	0.44230	0.26080	0.17510	0.38230	0.75311	0.903	2.263	3.834	0.118	0.097	0.086	0.061	0.069
	0.10	5.818	2.669	1.346	0.72240	0.44700	0.26060	0.17190	0.37410	0.74281	0.894	2.237	3.831	0.118	0.098	0.086	0.068	0.071
Solv.	5.880	2.683	1.350	0.72180	0.45050	0.26120	0.17010	0.37270	0.74071	0.885	2.220	3.828		0.099	0.087	0.060	0.078	
Rubidium bromide in glycerol.....	1.00	4.965	2.307	1.199	0.64830	0.39670	0.24570	0.20140	0.43350	0.83391	0.942	2.520	4.070	0.115	0.092	0.085	0.063	0.062
	0.75	5.177	2.393	1.228	0.66030	0.40410	0.24840	0.19310	0.41780	0.81461	0.914	2.474	4.025	0.116	0.095	0.086	0.063	0.063
	0.50	5.388	2.472	1.274	0.67890	0.41080	0.25280	0.18560	0.40440	0.78491	0.913	2.434	3.955	0.118	0.094	0.084	0.065	0.062
	0.25	5.623	2.565	1.284	0.69900	0.41460	0.25540	0.17780	0.38980	0.77851	0.930	2.412	3.915	0.114	0.099	0.084	0.069	0.062
	0.10	5.858	2.650	1.338	0.70960	0.42260	0.25990	0.17070	0.37730	0.74731	0.909	2.336	3.863	0.121	0.098	0.089	0.068	0.063
Solv.	5.885	2.664	1.358	0.71210	0.42590	0.26040	0.16990	0.37640	0.73591	0.904	2.348	3.840		0.096	0.091	0.067	0.068	
Rubidium iodide in glycerol.....	1.00	4.613	2.163	1.121	0.61840	0.37630	0.23550	0.20880	0.46230	0.89161	0.917	2.657	4.264	0.113	0.093	0.081	0.064	0.060
	0.75	4.912	2.292	1.181	0.64390	0.38920	0.24200	0.20360	0.43620	0.84681	0.954	2.569	4.132	0.114	0.096	0.083	0.065	0.061
	0.50	5.169	2.365	1.209	0.66850	0.39810	0.24720	0.19380	0.42280	0.82691	0.919	2.512	4.044	0.118	0.096	0.084	0.065	0.061
	0.25	5.566	2.554	1.294	0.69550	0.41320	0.25480	0.19790	0.39150	0.77291	0.922	2.420	3.924	0.118	0.097	0.084	0.070	0.062
	0.10	5.769	2.628	1.328	0.71020	0.42360	0.25660	0.17330	0.38040	0.75291	0.908	2.360	3.898	0.119	0.098	0.087	0.068	0.065
Solv.	5.854	2.669	1.341	0.71440	0.42430	0.25810	0.17080	0.37460	0.74571	0.900	2.357	3.874		0.099	0.088	0.068	0.064	
Rubidium nitrate in glycerol.....	0.50	4.639	2.355	1.204	0.65300	0.39820	0.24710	0.21560	0.42460	0.83071	0.931	2.511	4.046	0.097	0.096	0.084	0.064	0.061
	0.25	5.571	2.562	1.294	0.69550	0.41790	0.25610	0.17950	0.39180	0.77271	0.938	2.393	3.904	0.118	0.098	0.086	0.066	0.063
	0.10	5.787	2.634	1.338	0.70990	0.42370	0.25700	0.17280	0.37960	0.74731	0.909	2.360	3.891	0.120	0.097	0.088	0.068	0.064
	Solv.	5.854	2.669	1.341	0.71440	0.42430	0.25810	0.17080	0.37460	0.74571	0.900	2.357	3.874		0.099	0.088	0.068	0.064

\*Calc. from N.

TABLE 141.—*Viscosity and Fluidity of Ammonium Iodide and Rubidium Bromide in Various Mixtures.*

	Mol. conc.	$\eta$ 25°	$\eta$ 35°	$\eta$ 45°	$\phi$ 25°	$\phi$ 35°	$\phi$ 45°	Temperature coefficients.	
								25 to 35°	35 to 45°
Ammonium iodide in 75 per cent glycerol with water at 25°, 35°, 45°..	1.00	0.2548	0.1580	0.1049	3.925	6.327	9.529	0.0612	0.0506
	0.75	0.2703	0.1656	0.1094	3.700	6.039	9.138	0.0632	0.0513
	0.50	0.2873	0.1754	0.1143	3.481	5.700	8.749	0.0637	0.0535
	0.25	0.3058	0.1842	0.1193	3.270	5.429	8.383	0.0660	0.0544
	0.10	0.3097	0.1873	0.1204	3.229	5.338	8.302	0.0653	0.0555
	Solv.	0.3174	0.1902	0.1220	3.151	5.259	8.197	0.0669	0.0559
Ammonium iodide in 0 per cent glycerol with water at 25°, 35°, 45°..	1.00	0.05335	0.03838	0.02821	18.73	26.05	35.45	0.0390	0.0361
	0.75	0.05534	0.03950	0.02885	18.07	25.32	34.66	0.0401	0.0369
	0.50	0.05793	0.04089	0.02967	17.26	24.46	33.70	0.0417	0.0378
	0.25	0.06029	0.04230	0.03182	16.59	23.64	31.43	0.0425	0.0329
	0.10	0.06064	0.04260	0.03092	16.49	23.47	32.34	0.0423	0.0379
	Solv.	0.06174	0.04299	0.03092	16.20	23.26	32.34	0.0432	0.0390
Ammonium iodide in 25 per cent glycerol with water at 25°, 35°, 45°..	1.00	0.01802	0.01406	0.01124	55.49	71.12	88.97	0.0282	0.0251
	0.75	0.01843	0.01436	0.01147	54.26	69.64	87.18	0.0283	0.0252
	0.50	0.01910	0.01464	0.01157	52.36	68.31	86.43	0.0305	0.0265
	0.25	0.01973	0.01501	0.01180	50.68	66.62	84.75	0.0314	0.0272
	0.10	0.01997	0.01510	0.01182	50.07	66.22	84.60	0.0322	0.0278
	Solv.	0.02018	0.01525	0.01189	49.55	65.57	84.10	0.0333	0.0282
Ammonium iodide in water at 25°, 35°, 45°.....	1.00	0.00838	0.00695	0.00584	119.3	143.9	178.2	0.0206	0.0170
	0.75	0.00869	0.00701	0.00589	115.1	142.7	169.8	0.0240	0.0190
	0.50	0.00871	0.00705	0.00595	114.7	141.7	168.0	0.0235	0.0185
	0.25	0.00877	0.00712	0.00590	114.0	140.4	169.4	0.0232	0.0206
	0.10	0.00889	0.00717	0.00597	112.4	139.4	167.5	0.0240	0.0217
	Solv.	0.00891	0.00720	0.00597	112.2	138.9	167.5	0.0238	0.0205
Rubidium bromide in 75 per cent glycerol with water..	1.00	0.2753	0.1702	0.1137	3.627	5.874	8.797	0.0619	0.0496
	0.75	0.2844	0.1756	0.1152	3.516	5.604	8.683	0.0619	0.0525
	0.50	0.2944	0.1795	0.1169	3.396	5.570	8.556	0.0640	0.0536
	0.25	0.3036	0.1838	0.1168	3.293	5.441	8.558	0.0652	0.0573
	0.10	0.3108	0.1877	0.1184	3.217	5.327	8.432	0.0656	0.0583
	Solv.	0.3135	0.1880	0.1209	3.189	5.319	8.270	0.0668	0.0555
Rubidium bromide in 50 per cent glycerol with water.	1.00	0.05514	0.03958	0.02906	18.14	25.27	34.41	0.0393	0.0362
	0.75	0.05625	0.04035	0.02946	17.78	24.78	33.95	0.0394	0.0370
	0.50	0.05791	0.04064	0.03014	17.27	24.61	33.18	0.0425	0.0348
	0.25	0.05915	0.04194	0.03018	16.91	23.90	33.13	0.0414	0.0386
	0.10	0.05986	0.04207	0.03029	16.71	23.77	33.01	0.0423	0.0389
	Solv.	0.06021	0.04229	0.03035	16.61	23.65	32.95	0.0424	0.0393
Rubidium bromide in 25 per cent glycerol with water.	0.50	0.01931	0.01492	0.01179	51.80	67.03	84.81	0.0294	0.0265
	0.25	0.01970	0.01505	0.01186	50.76	66.44	84.30	0.0309	0.0269
	0.10	0.01996	0.01518	0.01190	50.09	65.88	84.06	0.0315	0.0276
	Solv.	0.02017	0.01523	0.01191	49.59	65.64	83.97	0.0324	0.0279
Rubidium bromide in water at 25°, 35°, 45°.....	0.50	0.00872	0.00718	0.00608	114.7	139.4	164.3	0.0215	0.0179
	0.25	0.00882	0.00720	0.00600	113.2	138.8	166.7	0.0226	0.0201
	0.10	0.00880	0.00717	0.00596	113.6	139.4	167.7	0.0227	0.0203
	Solv.	0.00891	0.00720	0.00597	112.2	138.9	167.5	0.0238	0.0205

TABLE 142.—*Percentage Increase in Fluidity of Normal Solutions in Glycerol at 25°, 35°, and 45°.*

	25°	35°	45°
NH <sub>4</sub> I...	32.4	28.4	22.9
RbI....	28.3	23.4	19.6
RbBr...	18.5	15.4	11.9
RbCl...	12.2	9.9	6.8

TABLE 143.—*Comparison of Percentage Increase in Fluidity of Glycerol by Ammonium Iodide and Rubidium Iodide at 25°.*

Mol. conc.	NH <sub>4</sub> I	RbI
1.00	32.4	26.3
0.75	22.2	19.2
0.50	13.9	13.1
0.25	6.0	5.2
0.10	1.1	1.5

TABLE 144.—Percentage Increase in Fluidity of Glycerol-Water Mixtures at 25°.

	Mol. conc.	Glycerol	75 p. ct.	50 p. ct.	25 p. ct.	Water
RbBr.....	1.0	18.5	11.2	9.2	(8.8)	(4.5)
NH <sub>4</sub> I.....	1.0	32.4	24.5	15.7	11.9	6.3

## DISCUSSION OF RESULTS.

The hypothesis of Dutoit and Aston, already referred to, makes the dissociating power of a solvent a function of its own association. The degree of association of a solvent by the method of Ramsay and Shields has been shown to decrease with rise in temperature. Therefore the increase in conductivity usually observed with rise in temperature can not be due to an increase in the number of ions present, but must be caused by an increase in the velocity of those ions. As Guy and Jones have already brought out, the change in the velocity of the ions with rise in temperature is to be ascribed to the change in the viscosity of the media surrounding the ions, and in some instances to the change in the mass of the ionic complexes formed by the ions and a certain number of molecules of the solvent.

Previous workers with glycerol as a solvent have already noted the enormous increase in the conductivity of solutions in it with rise in temperature. While Guy and Jones have found some evidence for the existence of glycerolates, we believe the chief conditioning factor to be the change in the viscosity of the solvent. It is with the viscosity phenomena, and chiefly with the lowering of the viscosity of glycerol by certain salts, that this investigation has had to deal.

Both conductivity and viscosity data have been obtained for the various salts and are given in tabular form with accompanying tables of temperature coefficients.

Tables 126 to 130, inclusive, contain the molecular conductivities at ten-degree intervals from 25° to 75° of ammonium iodide and of the several rubidium salts which have been studied in pure glycerol as a solvent. In agreement with the work of preceding investigators, viz, Jones and Schmidt, and Guy and Jones, all the values for  $\mu$ , are seen to be extremely low—much smaller than the corresponding values in water. These values show a marked increase with rise in temperature, and in the more dilute solutions (N/10 to N/1600) a regular increase with dilution. It is to be noted that in the more concentrated solutions, especially of the iodides, a decrease in conductivity takes place, the minimum lying as a rule close to the value for the N/10 solution. A discussion of this phenomenon will be taken up after a review of the viscosity data.

The corresponding temperature coefficients of all the salts studied, both in conductivity units and in percentages, are of the same order of magnitude and show the same relative increase with increased dilution. This is to be expected, since these salts are all binary electrolytes, and since all belong to that class whose cations, possessing the largest atomic volumes, have been shown to have little or no hydrating power in water. Such is not the case with ternary electrolytes in glycerol and especially with salts of calcium, strontium, barium, and cobalt, the explanation of which has been fully given by Guy and Jones, who base their conclusions on the solvate theory. They point out that if there is solvation this should be more marked in the more dilute solutions where the amount of solvent per ion is greatest. Hence a



change in temperature would produce the greatest effect where the solvation was greatest, viz, in the more dilute solutions, and in solutions of those salts which have the greatest power of solvation.

The per cent temperature coefficients are seen to be very large, being from 10 to 11 per cent between 25° and 35°. They decrease rapidly with rise in temperature, the values between 65° and 75° lying between 4.5 and 5 per cent. This may be partially accounted for by the enormous decrease in the viscosity of glycerol with rise in temperature. At 25° glycerol has a viscosity approximately 660 times that of water, while at 35° the value is 370 times that of water—but little more than half as great. At 75° the ratio falls to 70. In no other common solvent are the temperature coefficients of conductivity so great, and the above ratios will show to some extent why this should be the case.

Tables 131 to 138, inclusive, contain the molecular conductivities at 25°, 35°, and 45° of ammonium iodide and rubidium bromide in mixtures of glycerol with water. Figs. 81 and 82 express these results graphically. The solvents were prepared by diluting  $n$  c.c. of glycerol to 1 liter and denoting the resulting solvent as a mixture of  $n$  per cent glycerol with water.

It will be seen that the conductivity curves of such mixtures show a decided sagging, the conductivity values being always less than would be expected from the law of averages. The explanation of this has been given by Jones and Lindsay<sup>1</sup> and by Jones and Murray<sup>2</sup> for mixtures of water with the alcohols, and has been extended to mixtures containing glycerol by Guy and Jones. When two highly associated liquids are mixed, or, to take a specific instance, when glycerol is mixed with water, it has been shown that in such a

case the properties of the mixture are not additive, each solvent tending to break down the association of the other; the combined dissociating effect of the two being less than would be expected had there been no such mutual diminution of the association. Guy and Jones have shown that in the case of glycerol mixtures with the alcohols the diminution of the association takes place largely in the case of the glycerol.

In table 139 a comparison is made of the temperature coefficients at 25° to 35° of

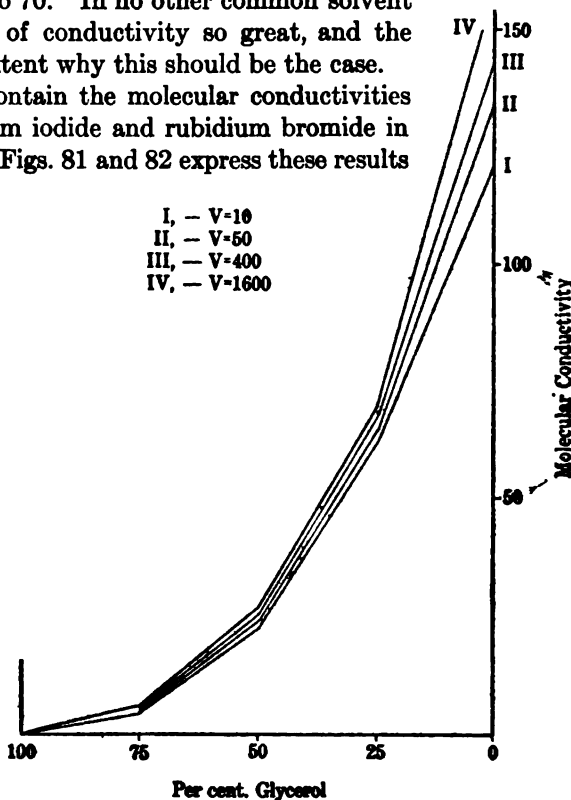


Fig. 81.—Conductivity of Ammonium Iodide in Glycerol-Water at 25°.

<sup>1</sup>Amer. Chem. Jour., 28, 329 (1902).

<sup>2</sup>Ibid., 30, 198 (1908).

the two salts which have been studied in mixed solvents. These are seen to diminish rapidly with the addition of water, passing from 10 per cent in pure glycerol to 2 per cent in 25 per cent glycerol.

The curve representing the specific conductivities of the various mixtures from glycerol to pure water is shown in fig. 83. The values for 50 and 25 per cent glycerol are larger than that for water. This is probably due to the presence of a few OH ions split off from the glycerol by action of the water.

#### NEGATIVE VISCOSITY COEFFICIENTS.

A historical sketch of previous work on viscosity has already been given. It is necessary, therefore, to take up here only the more important points.

Jones and Veazey's apparently satisfactory explanation of the phenomenon of negative viscosity coefficients has received ample corroboration by later workers. It will be remembered that they attributed the lowering of the viscosity of a solvent by a dissolved substance to the lessening of the skin friction between the molecules of the solvent and the molecules or ions of the solute in a given volume of the solution, because of the large atomic volumes of the cations, viz, potassium, rubidium, and caesium, these three metals occupying the maxima on the atomic-volume curve. Subsequent investigations have shown that certain ammonium salts in organic solvents, such as glycerol, are to be included in this category. Although we may not speak of the ammonium radicle  $\text{NH}_4$  as having atomic volume, still, it is well known that it possesses chemical properties closely allied to the alkali metals.

It is not surprising, therefore, to find negative viscosity effects produced by ammonium salts, and from observations made by Guy and Jones on ammonium bromide, and from our own observations on ammonium iodide, it is probable that the molecular complex  $(\text{NH}_4)$  should occupy a place on the volume curve close to rubidium.

In table 140 the viscosities and fluidities of ammonium iodide and of rubidium chloride, bromide, iodide, and nitrate<sup>1</sup> in pure glycerol at 25° to 75° are given for a range of dilution from N to N/10. In every case the viscosity of the solution is less

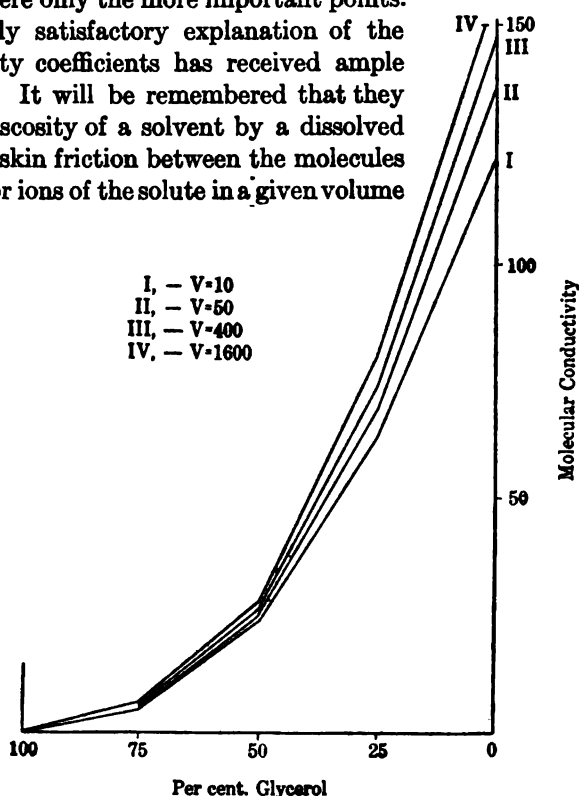


FIG. 82.—Conductivity of Rubidium Bromide in Glycerol-Water at 25°.

<sup>1</sup>N/123 sol. saturated at 20°.

than that of the solvent. Even at 75°, rubidium chloride, which increases the fluidity the least, shows a positive fluidity coefficient of 0.3 per cent for the N/10 solution.

A table of per cent temperature coefficients of fluidity is given with each table of viscosities. These are seen to be almost equal to the temperature coefficients of conductivity, but in every case are somewhat larger. This is to be accounted for by the decrease in association of the solvent with rise in temperature, causing a decrease in the ionization of the solute and therefore a smaller conductivity. This would in part offset the increase in conductivity due to an increase in the velocity of the ions, because of the decrease in the viscosity of the solvent with rise in temperature.

The greatest viscosity lowering or increase in fluidity is to be observed in the case of the normal solution. This is obvious, since the effect is proportional to the concentration. The dilution curve does not pass through a minimum, but becomes asymptotic to that of the solvent at dilutions beyond the N/50. The percentage increase in fluidity becomes less also with rise in temperature, which may be accounted for by the change in the molecular aggregates of the solvent and by the greater effect of temperature than of the dissolved salt on the viscosity of the solvent.

With the above facts in view, it is possible to explain the minima found at low temperatures in the conductivity curves for the concentrated solutions. These minima are more marked at 25°, and in the case of those salts which give the greatest lowering

of the viscosity of glycerol, viz, ammonium and rubidium iodides. In the concentrated solution (N-N/4) the ionization is nearly constant, while the negative viscosity effect decreases with increased dilution.

Reference to fig. 84 will show that the conductivity and fluidity curves at 25° for rubidium iodide are practically parallel up to and through the N/10 solution. Beyond that dilution the increased ionization causes a rise in the conductivity curve, while the fluidity curve becomes the asymptote of the solvent. Here we have conductivity varying directly as the fluidity or inversely as the viscosity. It is of interest to observe that a salt can lower the viscosity of a solvent to such an extent as to increase its own conductivity in that solvent. Fig. 85 shows similar results with ammonium iodide.

Table 142 shows the relative percentage increase in fluidity produced by normal

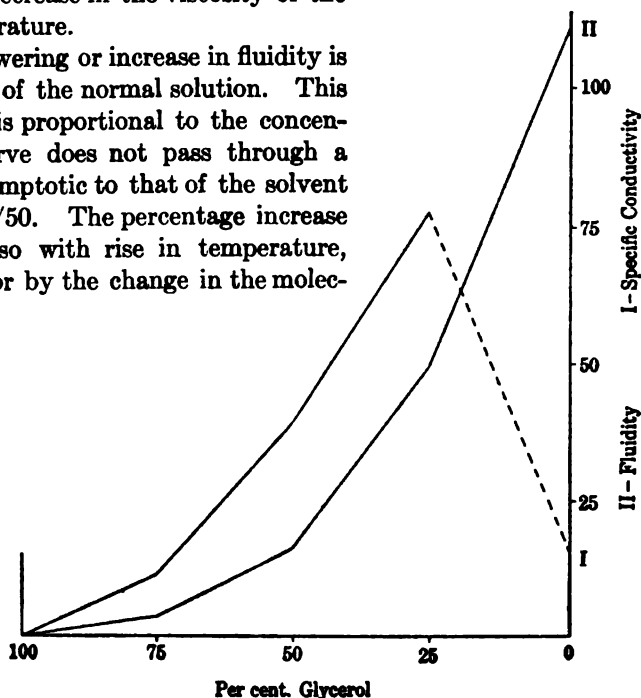


FIG. 83.—Specific Conductivity and Fluidity of Glycerol-Water Mixtures at 25°.

solutions of the various rubidium salts and of ammonium iodide at 25° to 45°. It is evident that of the halogen salts of rubidium the iodide produces the greatest change in fluidity, followed by the bromide, then the chloride. This may be explained by the fact that when the cation, here rubidium, to which the increase in fluidity is mainly due, remains the same, the negative viscosity effect is a function of the molecular volumes of the salt in question.

If we divide the molecular weights of the three halogen salts by their densities referred to water as a unit, we obtain the following values:

$$\text{RbI}, \frac{212.37}{3.02} = 7.02; \quad \text{RbBr}, \frac{165.37}{2.78} = 5.95; \quad \text{RbCl}, \frac{120.91}{2.20} = 5.496.$$

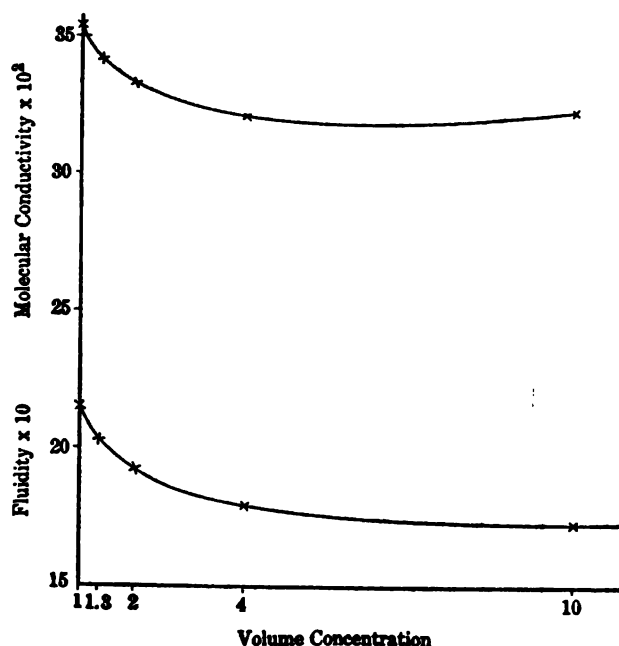


FIG. 84.—Conductivity and Fluidity of Rubidium Iodide in Glycerol at 25°.

Reference to table 142 will show that the experimental data are in accord with this; rubidium iodide at 25° producing a per cent increase in fluidity of 26.3, rubidium bromide 18.5, and rubidium chloride 12.2. It was impossible to prepare a normal solution of rubidium nitrate in glycerol at the temperature 20°. The N/2 solution was nearly saturated at that temperature, and shows somewhat greater negative viscosity coefficients than would be expected.

The N/4 solution, however, gives values between that of rubidium bromide and iodide, which is to be expected from its molecular volume. No adequate explanation can be offered for the apparently abnormal negative viscosity coefficients of ammonium iodide in glycerol.

In table 143 is given the percentage increase in fluidity at 25° produced by the two salts showing the most marked negative viscosity effect, viz, rubidium iodide

and ammonium iodide over the range of dilution studied. That the increase in fluidity is not exactly proportional to the concentration, may be due to the slight increase in ionization in the more dilute solution, the effect of the anions tending to offset that of the cation.

Table 141 shows the viscosities and fluidities of rubidium bromide and ammonium iodide in glycerol-water mixtures at 25°, 35°, and 45°. The addition of water to glycerol causes an enormous increase in fluidity. The curve representing the fluidity changes with decreasing percentages of glycerol is strikingly similar to the conductivity curves in those mixtures.

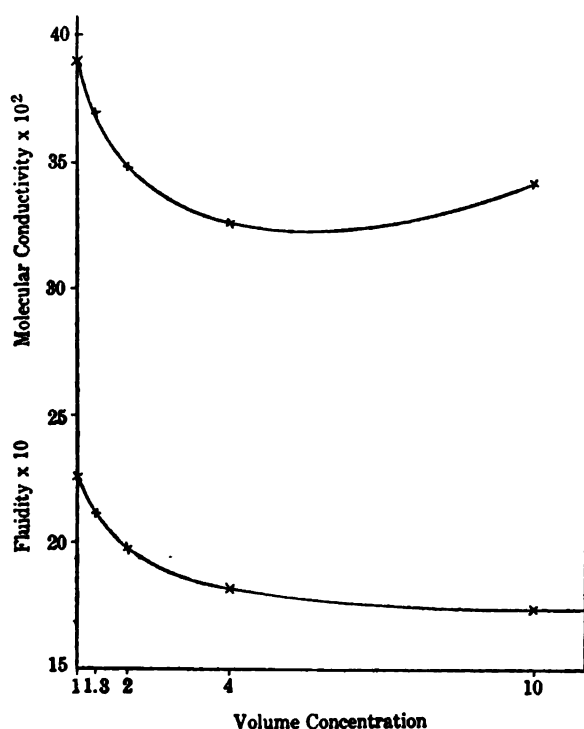


FIG. 85.—Conductivity and Fluidity of Ammonium Iodide in Glycerol at 25°.

The salts studied show negative viscosity in the glycerol-water mixtures and in pure water at low temperatures. In water at 45°, rubidium bromide shows a tendency to pass over to positive viscosity, although the transition is not very marked.

The last table (144) gives a comparison of the percentage increase in fluidity produced by normal solutions of the two salts in glycerol-water mixtures at 25°. The values do not follow the law of averages in such mixtures, but are lower. This is in all probability due to the increased ionization in the mixed solvents, and also to the breaking down of the molecular complexes of the solvent, which would in both cases give ultimate particles with greater frictional surfaces.

## SUMMARY.

The following points have either been confirmed or brought out:

1. Conductivity values in glycerol are extremely small, but show regular increase with rise in temperature and, except in special cases, with dilution.
2. In the cases of salts producing a marked lowering of the viscosity of the solvent, a minimum in the conductivity curve of the concentrated solutions has been noted, the conductivity varying directly with the fluidity.
3. Conductivities in glycerol-water mixtures do not follow the law of averages, but are always lower.
4. Rubidium salts produce a phenomenal lowering of the viscosity of glycerol, much greater than that of the corresponding potassium salts.
5. Ammonium salts seem more closely allied to rubidium than to potassium in their effect on the viscosity of a solvent like glycerol.
6. The percentage increase in fluidity of the solvent produced by the dissolved salt becomes less with rise in temperature and with dilution.
7. Rubidium salts in pure glycerol show no tendency to produce positive viscosity even at 75°.
8. Curves representing fluidity and conductivity in mixtures of glycerol and water show marked similarity over the range of temperature studied.

## GENERAL DISCUSSION OF THE RESULTS.

### RESULTS OBTAINED BY STINE.

When this work was undertaken by Dr. Stine the suggestion that we have hydration in aqueous solution was about six years old.<sup>1</sup> Jones and Ota<sup>2</sup> and Jones and Knight<sup>3</sup> had observed the abnormally great depression of the freezing-point of water produced by certain electrolytes, and Jones and Chambers<sup>1</sup> had taken up a systematic study of a few substances in this connection. This work was continued at the suggestion of Jones by Chambers and Frazer,<sup>4</sup> and it was found soon that the phenomenon in question is of a more or less general character.

This problem was then taken up systematically and in a broad way for the first time by Jones and Getman.<sup>5</sup> They studied carefully a large number of typical substances, and found the apparently abnormally great freezing-point lowering to be a general phenomenon. This was later made more comprehensive by Jones and Bassett.<sup>6</sup>

A method was worked out during this period for calculating the approximate composition of the hydrates formed by the more common electrolytes, over a wide range of dilution; and such calculations were made for a large number of substances. At the time the work recorded in this monograph was undertaken by Dr. Stine, we knew the approximate hydrating power at different dilutions of many of the substances with which we have to deal in the chemical laboratory.

The problem which Dr. Stine solved (and when we consider the number of factors involved, solved very successfully) was the effect of one salt on the hydrating power of another salt present in the same solution. That the problem was of necessity very complex can be seen from a moment's consideration. If we mix two salts with a common ion, as is well known, each salt drives back the dissociation of the other. This alone complicates the problem tremendously; further, that conductivity is not an accurate measure of dissociation in concentrated solutions also complicates the problem.

The first pair of substances studied contained a salt with large hydrating power—calcium chloride, and one with very small hydrating power—potassium chloride.

It was found that the amount of water combined increases with increase in concentration in the mixture as in the separate solutions; yet the total amount of water combined with the calcium chloride is less when potassium chloride is present. This is but the application of the effect of mass. The mixture of calcium chloride and potassium chloride contains less water than a solution of calcium chloride of the same concentration. We find in the case of the mixture, as in that of the simple salt, that the number of gram-molecules of combined water increases with the con-

<sup>1</sup>Amer. Chem. Journ., 23, 103 (1900).

<sup>2</sup>Ibid., 23 (1899).

<sup>3</sup>Ibid., 23, 110 (1899).

<sup>4</sup>Ibid., 23, 512 (1900).

<sup>5</sup>Carnegie Institution of Washington Publication No. 88.

<sup>6</sup>Zeit. phys. Chem., 46, 244 (1903); Phys. Rev., 18, 146 (1904).

centration; while the number of molecules of water combined with one molecule of the dissolved substance increases with the dilution of the solution.

The difference between the amount of water combined with the calcium chloride when alone, and when in the presence of potassium chloride, increases with the concentration of the two salts present.

The next system studied was a pair of salts both having large hydrating power and also approximately the same hydrating power. The salts chosen were calcium chloride and magnesium chloride. It was soon found, as would be expected from the effect of mass action, that each of these salts exerted a hydrating action upon the other, and that each was combined with less water when the two were mixed than when they were separate. The magnitude of the hydrating effect of each of these salts on the other was worked out quantitatively.

The following ternary systems were also studied in the above connection: Magnesium chloride and strontium chloride, magnesium nitrate and strontium nitrate, and magnesium nitrate and calcium nitrate. Results of the same general character were obtained with these substances as with those already mentioned. Each salt diminishes the hydration of the other, and the magnitude of this effect was worked out approximately.

A pair of binary electrolytes (sodium bromide+lithium bromide) and a pair of quaternary electrolytes (aluminium chloride+ferric chloride) were studied in this connection. Results of the same general character were obtained as with the ternary electrolytes. The results with the quaternary electrolytes are somewhat complicated by the hydrolysis of these substances, especially in the more dilute solutions. Nevertheless, the effect of each salt in dehydrating the other is clearly shown from the freezing-point determinations.

The work was then extended from pairs of salts with a common anion to pairs with a common cation. The salts used were calcium chloride and calcium nitrate, and the results are similar to those obtained when the anion was kept constant.

Another problem that was studied by Stine was the effect of temperature on the conductivities of solutions of electrolytes and of mixtures of these solutions. For this purpose it was necessary to select salts that do not form double salts with one another, and which have little or no power to combine with water. The salts chosen were potassium chloride and ammonium chloride.

The conductivities of potassium chloride and of ammonium chloride were determined separately, and then the conductivities of the mixtures taken. The conductivities of the mixtures are less than the sum of the conductivities of the individual salts, as would be expected from the fact that each of the two salts with a common ion suppresses the ionization of the other.

If this were the only cause of the difference, then this difference should be greatest when the most strongly dissociated solutions are mixed. This difference should, therefore, be greater at 0° than at 12°, and greater at 12° than at 25°. Exactly the opposite is true.

Again, if this difference is dependent only upon the amount of the dissociation, and the driving back of the dissociation of one salt by another salt with a common ion, then, since the change in dissociation from 0° to 12° is a little greater than



from 12° to 25°, we should expect to find the difference in question greater from 0° to 12° than from 12° to 25°. Here, again, exactly the opposite is true.

The difference between the conductivity of the mixed salts and the sum of the conductivities of the constituents can not, then, be accounted for as due solely to a change in dissociation caused by each salt driving back the dissociation of the other with a common ion. Stine pointed out that there are three other factors which must be taken into account: (1) change in hydration, which changes the size and mass of the ion; (2) change in the viscosity of the solution with change in temperature, which changes the friction of the ions in moving through the solution; (3) change in the number of dissolved particles—ions and molecules.

In the cases of potassium and ammonium chlorides, which are very little hydrated, the first factor (change in hydration) plays a very minor rôle; the third undoubtedly plays some part, since  $\alpha$  becomes smaller the higher the temperature; the second, or change in viscosity with rise in temperature, is undoubtedly the most important.

The effect of the viscosity of the solvent on the conductivity of electrolytes dissolved in that solvent was thus clearly recognized by Stine, and pointed out by him a half-dozen years ago.

This work was strong evidence for the solvate theory of solution. It showed that the effect of one salt on the hydration of another salt with which it was mixed was what would be expected from the law of mass action. This was worked out for a sufficient number of typical substances, with very different hydrating powers, to enable us to draw a general conclusion as to the correctness of the solvate theory of solution. In some cases there are apparent discrepancies between the results obtained by Stine and those found by subsequent workers with the same substances. It must be remembered that the subsequent work with both the freezing-point and the conductivity methods was done after these methods were both greatly improved.

Further, in the work of Stine the aim was to obtain comparative values for the different substances rather than the highest degree of accuracy for the individual compounds.

#### RESULTS OBTAINED BY PEARCE.

The work which had already been done<sup>1</sup> in this laboratory on the freezing-point lowerings of water produced by electrolytes in general, had shown that they practically all give so-called "abnormal lowerings"—that is, lowerings much greater than can be accounted for from their dissociation. These freezing-point lowerings become more and more abnormal the more concentrated the solution.

On the other hand, Jones,<sup>2</sup> when working in Ostwald's laboratory, had used the freezing-point method to measure the dissociation of dilute solutions of electrolytes. This was done for the purpose of seeing whether the freezing-point and conductivity methods gave the same or different values for the dissociations of electrolytes in dilute solutions, or whether the so-called solubility method of measuring dissociation gave the true values. It was subsequently shown that the last-named method gave incorrect results.

The freezing-point method, as used by Jones in 1892, gave values for dissociation that agreed fairly well with those calculated from the conductivity measurements of Kohlrausch. It was not known at that time that concentrated solutions of these

<sup>1</sup>Carnegie Institution of Washington Publication No. 60.

<sup>2</sup>Zeit. phys. Chem., 11, 110, 529; 12, 622 (1893).

same electrolytes would give such abnormally great lowerings of the freezing-point of water. After this fact was brought to light in my laboratory, the question arose whether we can use the freezing-point method as an accurate measure of dissociation at any dilution. To test this point Dr. Pearce carried out the elaborate investigation recorded in this monograph. The dissociations of a large number of electrolytes were measured by the freezing-point method, and the results were compared with those obtained by the conductivity method. For this purpose the freezing-point method must be improved as much as possible and all sources of error reduced to a minimum. The results recorded in this chapter are to be regarded as among the most reliable freezing-point measurements that have been made. Similarly, the conductivity results are among the most accurate that had been obtained up to that time. The conductivity method and apparatus have subsequently been somewhat improved, yet the agreement between the values obtained by Pearce and those of subsequent work<sup>1</sup> are, in general, very good. This investigation, in which the dissociation was measured by both the freezing-point and the conductivity methods, ought to show to what extent each method is influenced by the hydration of the ions. It ought also to throw some light upon the effect of hydration on the relative velocities of the ions.

It would seem on *a priori* grounds that hydration ought to affect the freezing-point method more than the conductivity method as a means of measuring electrolytic dissociation. If a part of the water is combined with the dissolved substance, this is removed from the field of action as far as solvent is concerned. Freezing-point lowering is an arithmetical property. It depends upon the ratio between the number of molecules of the dissolved substance and those of the solvent. Freezing-point lowering would, therefore, be affected directly by any loss in solvent water due to a combination of a part of the water with the substance dissolved in it.

The conductivity method of measuring dissociation would also be affected by water of hydration. The hydrated ions would have greater mass than the unhydrated, and their velocities would, therefore, be less. Hydration would also have some effect on the viscosity of the solution. Taking all of these factors into account, it would seem that hydration would affect the freezing-point method more than the conductivity method, and dissociation as measured by freezing-point lowering ought to have slightly higher values than as measured by conductivity. We shall see whether or not this is the case.

Pearce also determined the freezing-point lowerings produced by concentrated solutions of the electrolytes with which he worked, and from the results calculated the approximate compositions of the hydrates formed by these substances at the various dilutions. Pearce worked especially with strongly hydrated substances, such as the chlorides of calcium, strontium, barium, and magnesium, and with the nitrates of these same elements. From the results with these substances it seemed that dissociation as measured by the freezing-point method was slightly greater than as measured by conductivity. This work was extended to the chloride and nitrate of cobalt, the chloride and nitrate of copper, and nickel nitrate. From these results it would seem that the molecular hydration and the total amount of combined

water are the same for any two salts, such as the above, which contain a common cation. From these results it therefore appears probable that the *hydrating power of a salt is dependent chiefly upon the cation*.

The quaternary electrolyte aluminium chloride and the binary electrolyte sodium bromide were also brought within the scope of this work. It was also extended to the strong mineral acids, hydrochloric, nitric, and sulphuric. This work included fifteen salts and three strong acids, over a range of dilution from 0.01 to 2.0 normal. The results seem to justify the following conclusions:

In the more dilute solutions we have mainly ions present; in the more concentrated, largely molecules. We could thus study the effects of ions and molecules on freezing-point lowering.

The hydration, or number of molecules of water combined with one molecule of the salt, or the ions resulting from it, increases with the dilution. This, in very dilute solutions, becomes of a large order of magnitude. The ions, thus largely hydrated in very dilute solutions, move more slowly than unhydrated ions, and the dissociation as measured by the conductivity method would thus be too small.

The decrease in the number of molecules of water combined with one of the dissolved substances is in keeping with the work on the absorption spectra of solutions which has been in progress in this laboratory for the past seven years, and upon which several monographs<sup>1</sup> have already been published by the Carnegie Institution of Washington. The resonators in the more concentrated solutions are much freer to vibrate than in the more dilute—they are less hydrated.

The most interesting and important point established in this investigation is that the hydrating power of a salt is a function chiefly of the *cation*, and the relation between hydrating power and atomic or ionic volume. Anions may have some hydrating power, but it seems to be very slight.

At the highest maxima of the atomic-volume curve are the elements potassium, rubidium, and caesium. These elements with the largest atomic volumes form salts with small amounts of water of crystallization. These elements have very small hydrating power. Sodium and lithium also occupy maxima on the atomic volume curve, but these maxima are much lower than those of the three elements previously mentioned. Salts of sodium and lithium crystallize with two or three molecules of water, and these salts have some hydrating power.

Barium (with the largest atomic volume of the alkaline earths) forms salts which crystallize with two molecules of water. It has the smallest hydrating power of the alkaline earths. Calcium, strontium, and magnesium have smaller atomic volumes, form salts that crystallize with six molecules of water, and, therefore, have much larger hydrating power than barium. Magnesium, having the smallest atomic volume of this group, has the largest hydrating power.

Iron, cobalt, copper, and aluminium have very small atomic volumes and very large hydrating power.

A study of all the data obtained in this work shows not only that hydration is primarily a function of the cation, but *varies inversely as the atomic volume of the cation*; the smaller the cation the greater its hydrating power.

<sup>1</sup>Carnegie Institution of Washington Publications Nos. 60, 110, 130, and 160.

The discovery of this fact enabled us to explain many things which had hitherto been found in connection with the relative velocities of the ions, but which could not be explained. If we compare the atomic-volume curve with the curve of the migration velocities of the ions, we shall see that those ions which have the greatest hydrating power have the smallest migration velocities. Sodium and lithium, whose atomic volumes are less than half that of potassium, have velocities which are only about two-thirds that of potassium. This for a time was not understood. Sodium and lithium form salts which crystallize with two and three molecules of water; salts of these elements are therefore hydrated in solution, and these hydrates around the sodium and lithium ions decrease the velocities of those ions.

A large number of lines of evidence for the above relations are discussed in the preceding pages. The values of  $\alpha$  are calculated from the molecular lowerings of the freezing-point, for all concentrations less than that at which the freezing-point curve passes through the minimum. In the more concentrated solutions  $\alpha$  can not be calculated from freezing-point lowerings, on account of hydration.

It was predicted from the solvate theory of solution that dissociation as measured by the freezing-point method would have higher values than when measured by electrical conductivity. This was confirmed experimentally without a single exception.

In the case of every salt studied the dissociation as calculated from the freezing-point lowering is higher than the dissociation as calculated from conductivity.

Since the above prediction was based upon the solvate theory of solution, its verification is in keeping with that theory.

#### RESULTS OBTAINED BY KREIDER.

The conductivity method as left by Kohlrausch could not be satisfactorily used to measure dissociation in any solvent other than water. The reason for this is almost obvious. Take a solvent with small dissociation power. The dilution at which complete dissociation would be reached in such a solvent would be so great that the Kohlrausch conductivity method could not be applied to it. It would thus be impossible to determine  $\mu_{\infty}$  accurately for the substance in a slightly dissociating solvent. The result was that the conductivity method, as a means of measuring dissociation, could not be used with any reasonable degree of accuracy even with a solvent with the dissociating power of ethyl alcohol. We had, up to this time, no thoroughly reliable method for measuring the dissociation in such common and important solvents as the alcohols. The freezing-point method, obviously, could not be used for this purpose, since the alcohols do not freeze at temperatures that can be accurately measured.

The boiling-point method was the only one available for the purpose under discussion, and this could be used only with fairly concentrated solutions. Dilute solutions raised the boiling-point of alcohol so little that the change could not possibly be measured with any degree of accuracy. This is especially true since the boiling-point method is affected very seriously by barometric changes. Further, the rise in the boiling-point of a solvent like the alcohols, by a dissolved substance, is very slight; and, consequently, the error in measuring this small quantity is relatively large. The hope of measuring with reasonable accuracy dissociation in non-

aqueous solvents lies in improving the conductivity method until it can be used for this purpose. With this idea in mind, better forms of induction coils were constructed, and longer and more sensitive bridges employed. The rheostats were of high grade and very carefully calibrated. More important, however, than any of these improvements are those in the conductivity cells themselves. A form of cell which had a constant less than three units, was devised. This was secured by using platinum electrodes with large surfaces and placing these close together. The form, as already stated, was concentric platinum cylinders. It was necessary to take special precautions to purify the solvents, since work must be done in them in very dilute solutions. Kreider extended his work also to mixed solvents—mixtures of methyl and ethyl alcohols with water. The salts studied in pure methyl and pure ethyl alcohols are potassium iodide, ammonium bromide, potassium sulphocyanate, lithium nitrate, sodium iodide, calcium nitrate, cobalt chloride, and copper chloride.

Maxima in the molecular conductivities were found, the dilutions studied ranging, in general, from  $v=1,000$  to  $v=50,000$ .  $\mu_{\infty}$  was usually reached at a greater concentration at  $0^{\circ}$  than at  $25^{\circ}$ . This is what would be expected, since dissociation diminishes with rise in temperature. In some cases, however, the maxima occur at the same concentration at both temperatures.

A relation was found between the values of  $\mu_{\infty}$  in methyl and in ethyl alcohols, which is of interest. Take any given salt and divide the value of  $\mu_{\infty}$  for that salt in methyl alcohol by the value of  $\mu_{\infty}$  for that salt in ethyl alcohol, and the result is nearly a constant.

$$\frac{\mu_{\infty} \text{ methyl alcohol}}{\mu_{\infty} \text{ ethyl alcohol}} = \text{constant.}$$

The value of this constant for methyl and ethyl alcohols is very nearly 2.37. For cobalt chloride the constant came out 3.68, which is just about one and a half times 2.37. Jones<sup>1</sup> had previously determined the dissociation of certain salts in methyl and ethyl alcohols by the boiling-point method as improved by himself. If we divide the dissociation in methyl alcohol by that in ethyl alcohol, we obtain an average ratio which is very close to 2.37.

Dissociation as measured by conductivity in this work is greater than as found by the boiling-point method. This may be due, in part, to the polymerization of the undissociated molecules in the solvent in question. With the improved conductivity method used in this work it was possible in most cases to reach the true value of  $\mu_{\infty}$  for the dissolved substances; and, therefore, the conductivity method could be used to measure dissociation in some non-aqueous solvents.

The second investigation carried out by Dr. Kreider was an extension of the first to the compounds sodium bromide, lithium bromide, and cobalt bromide. Better methyl alcohol was obtained in this than in the former work, and dilutions as great as 100,000 liters were studied.

The relation earlier discovered between  $\mu_{\infty}$  in methyl alcohol and in ethyl alcohol was confirmed by this second investigation. When a salt is completely dissociated in each of two solvents, we have for the same concentration the same number of

<sup>1</sup>Zeit. phys. Chem., 31, 114 (1899).

ions in the two solutions. Conductivity is a function of the number of the ions and the velocities with which they move. When the numbers are constant we eliminate this factor, and conductivity is then a function of the relative velocities of the ions. The velocity is conditioned by the mass and volume of the ions, and by the fluidity, which is the reciprocal of the viscosity of the solvent. If the masses and volumes of the ions in two different solvents are constant, then ionic velocities in the two solvents should vary as the fluidities of these solvents. The ratio between  $\mu_{\infty}$  in the two solvents should be the same as the ratio between the fluidities of these solvents. This, however, was found not to be the case. This shows that the mass and probably the volume of the solvated ion must differ in the solutions in the two solvents. The ratio between the values of  $\mu_{\infty}$  in two solvents, when compared with the ratio of their fluidities, gives some idea of the relative solvation of the ion in question in the two solvents.

#### RESULTS OBTAINED BY MAHIN.

A fairly large amount of work had been done in my laboratory on the condition of salts in binary mixtures of certain solvents. The first work by Dr. Mahin had to do with the condition of salts in ternary mixtures of solvents, such as water, methyl alcohol, ethyl alcohol, and acetone. It was, of course, impossible to predict in advance whether any new principles would come to light as the result of the mutual action of three solvents upon one another. The salt used for this work was lithium nitrate. The conductivity of this salt in varying ternary mixtures of the above-named solvents was measured over a wide range in dilution. The viscosities of a number of these mixtures were also determined at 0° and 25°, and for various percentages of acetone, methyl alcohol, and water, of acetone, ethyl alcohol, and water, and for methyl alcohol, ethyl alcohol, and water.

It would seem, from this preliminary work with ternary mixtures of the various solvents, that the conductivities and viscosities are about what would be expected from the solutions in binary mixtures of these same solvents. Further work is being done in my laboratory on the properties of salts in ternary mixtures of these various solvents. Acetone is an unusual solvent in most of its properties. Substances dissolved in acetone are largely polymerized and, at the same time, some of the molecules are broken down into ions. This has led to confusion, in that it has been assumed that solutions in acetone as the solvent do not conduct themselves as solutions in other solvents. Jones carefully studied the point raised by Dutoit and Frederick, that certain substances dissolved in acetone have normal molecular weights, and yet show very considerable conductivity. These were found not to have normal molecular weights in acetone at any dilution that could be studied by the boiling-point method. It seemed highly desirable to measure the conductivities of substances dissolved in acetone over as wide a range of dilution as was possible. At very high dilutions the associate molecules should break down into simple molecules, and these then dissociate in the usual way.

Acetone is, furthermore, a solvent with *small* viscosity, and the viscosities of mixtures of acetone with the alcohols and with water were determined. The conductivities of solutions of salts in these mixtures were also measured at various

temperatures, and the temperature coefficients calculated. The curves for conductivity and fluidity could then be compared, and we could see whether the minima in the one corresponded to the minima in the other.

The questions raised were: Will those salts with small molecular conductivities when completely dissociated give value of  $\mu_{\infty}$  which are inversely proportional to viscosity; whether the product of viscosity is a constant for mixed solvents and at different temperatures? Is this value the same for different electrolytes?

The salts used were lithium nitrate and cadmium iodide. It is well known that acetone has very considerable dissociating power. It was found that lithium nitrate was practically completely dissociated in acetone at a volume of 100,000 liters. The Ostwald dilution law was tested as to its applicability to the results in acetone, and found, for the more dilute solutions, to hold approximately. The molecular conductivity was multiplied by the viscosity to see whether the product is, or is not, a constant. It was found that the product is practically constant and has the value of 0.70. This agrees with Walden's value in many organic solvents. In mixtures of water with acetone this value ranges from 0.60 to unity. The deviation of the value from 0.70 is probably due to the fact that complete dissociation was not always reached in acetone.

The molecular weight of lithium acetate in acetone was then determined by the boiling-point method, using the apparatus devised by Jones.<sup>1</sup> It was found for the most dilute solution that could be studied by this method that the molecular weight was greater than the theoretical for the simplest chemical formula. This shows that even in such solutions there is considerable polymerization of the molecules. This is in keeping with the earlier work of Jones, in which he determined the molecular weights of certain salts dissolved in acetone, and found that they were always polymerized by this solvent.

Cadmium iodide, which had also been found by Jones to be polymerized in acetone, was brought within the scope of this work. Although cadmium iodide is so little dissociated in water, we seem to have reached very nearly the value of  $\mu_{\infty}$  in acetone. The Ostwald dilution law holds roughly for dilute solutions of cadmium iodide in acetone, showing that  $\mu_{\infty}$  was nearly attained. This, however, required a dilution of several hundred thousand liters.

The dissociation of cadmium iodide in acetone is much greater at zero than at 25°. From our results it seems that the dissociation would probably be complete at about 600,000 to 700,000 liters. At this dilution the curves of molecular conductivity would become similar to those of fluidity, molecular conductivity and viscosity being inversely proportional to one another. The product of the two would then be a constant.

#### RESULTS OBTAINED BY SCHMIDT.

The work up to this point had had to do with solvents like the alcohols and acetone, which have viscosities of the same order of magnitude as water. The relations already discussed in this and in the preceding monograph<sup>2</sup> dealing with this same general subject had then been worked out for solvents having comparable viscosities.

<sup>1</sup>Amer. Chem. Journ., 19, 581 (1897).

<sup>2</sup>Carnegie Institution of Washington Publication No. 80.

The question then arose whether these same relations would hold for a solvent with a very large viscosity.<sup>1</sup> Fortunately there is one such solvent, glycerol, which is well adapted to this work. It has very high viscosity, is an excellent solvent, and has a fairly high dielectric constant, which means that it is a good dissociating agent. Further, it is a fairly strongly associated solvent, which also indicates that it would have considerable dissociating power.

An examination of the literature showed that very little had been done on the physical chemistry of glycerol. A few measurements of the conductivities of certain salts in glycerol had been made, but had not been carried out at all systematically. A similar condition was found to exist in reference to the measurements of the viscosities of solutions in glycerol as the solvent.

A number of details had to be carefully observed in working with such a viscous solvent as glycerol. These have already been discussed at sufficient length.

The salts studied in this first investigation in glycerol as a solvent were lithium bromide, potassium iodide, and cobalt chloride. These were studied in glycerol, water, methyl alcohol, ethyl alcohol, and in mixtures of glycerol with these solvents.

The curves show that the conductivities of these salts in the mixed solvents do not obey the law of averages. There is a marked sagging of the curves. There is no minimum in the conductivity curves, as was found with mixtures of alcohol and water. With cobalt chloride, results were obtained analogous in all essential particulars to those found for lithium bromide. Cobalt chloride has a greater conductivity than lithium bromide in glycerol. This is what would be expected, since the former is a ternary and the second a binary electrolyte. The conductivity of cobalt chloride in ethyl alcohol is, however, apparently abnormally low. This is due to polymerization of the cobalt chloride by the alcohol, as was shown by the molecular weight determination by the boiling-point method. The results with potassium iodide are similar to those obtained with lithium bromide.

Our work was carried out at different temperatures, so that the temperature coefficients of conductivity could be calculated. The most striking feature of the conductivities of salts in glycerol as a solvent is the enormous magnitude of the temperature coefficients. This amounts to more than 10 per cent per degree between 25° and 35°, and to more than 8.5 per cent between 25° and 45°. This is by far the largest temperature coefficient of conductivity that has ever been observed in any solvent. We shall see that it is closely related to the temperature coefficients of fluidity in this same solvent. The enormous increase in conductivity with rise in temperature is, therefore, due largely to the *rapid decrease in the viscosity of glycerol* as the temperature is raised.

The temperature coefficients of conductivity in the mixtures of glycerol with the other solvents, like the conductivities themselves, do not in any case obey the law of averages. They are always less than the average.

Glycerol is therefore a solvent which, with other solvents, gives a mixture whose properties are not additive, and in this respect glycerol resembles water. It has been shown by earlier work<sup>1</sup> that when water and the alcohols are mixed each diminishes the association of the other. A similar result manifests itself when glycerol is mixed with water or with the alcohols. Glycerol has the power of diminishing

<sup>1</sup>Carnegie Institution of Washington Publication No. 80.



the association of water and other associated solvents, such as the alcohols, and in turn these probably diminish the association of the glycerol. When the association of a solvent is diminished, so also is its dissociating power.

The viscosities of solutions of the above substances in glycerol and in mixtures of glycerol with water, with methyl alcohol, and with ethyl alcohol, at 25° and 35°, were measured. This enables us to calculate the temperature coefficients of viscosity or its reciprocal fluidity, and to compare the coefficients of fluidity with those of conductivity. The fluidities of tenth-normal solutions were measured and were in nearly all cases less than those of the corresponding solvents. Negative viscosity coefficients were, however, found for potassium iodide in water and in the 25 and 50 per cent mixtures of glycerol and water at 25° and 35°. The measuring of negative viscosity coefficients has already been discussed by Jones and Veazey.<sup>1</sup> While the salt does not lower the viscosity of glycerol itself, it does lower the viscosity of a 50 per cent mixture of glycerol and water.

The relation pointed out by Jones and Veazey is that only salts of metals with large atomic volumes lower the viscosity of the solvent in which they are dissolved. Although no salt was found which decreased the viscosity of pure glycerol, yet a relation was discovered which was analogous to that found in aqueous solutions. The effect of the several salts on the viscosity of glycerol is inversely proportional to the molecular volumes of the salts in question. Thus, potassium iodide increases the viscosity of glycerol less than lithium bromide, and the former has a much larger molecular volume than the latter. Cobalt chloride increases the viscosity of glycerol more than either of the other salts named, and cobalt chloride has the smallest molecular volume of the three. These relations are strictly analogous to those already discussed by Jones and Veazey<sup>1</sup> for solutions in water as the solvent.

Although glycerol is more than 1,000 times more viscous than methyl alcohol, yet the same relations seem to hold here as for the less viscous solvents. The fluidity curves for glycerol and water, and glycerol and the alcohols, resemble very closely the conductivity curves in these solvents. These curves show the same sagging below the straight line of averages, and have no minima.

The temperature coefficient of fluidity in pure glycerol, between 25° and 35°, is 11.5. This is slightly greater than the temperature coefficient of conductivity over this range of temperature, which is about 10.5 per cent. The larger value of the temperature coefficient of fluidity is probably due in part to the decrease in dissociation with rise in temperature, the molecules having less frictional surfaces than the ions into which they dissociate.

A comparison of the conductivity and fluidity curves in glycerol show, then, that the two phenomena run nearly parallel; glycerol, therefore, resembles water much more closely than it resembles the alcohols.

The molecular conductivities in glycerol do not reach the limiting value at any of the dilutions studied. At four-hundredth normal the molecular conductivities increase very slowly, showing that complete dissociation is reached at moderate dilution. Glycerol is, then, a strongly dissociating solvent, as would be expected from its large dielectric constant.

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<sup>1</sup>Carnegie Institution of Washington Publication No. 80.

It was found that  $\mu_{\infty}$  for glycerol, multiplied by  $\eta$ , the viscosity, gave the value 2.22 at 25° and 2.10 at 35°. Walden found a constant value of this product for about 30 organic solvents; but water, having the value 1.0, and glycol the value 1.32, were exceptions; glycerol is another exception. This may be due to the presence of the three hydroxyl groups, since water with one and glycol with two hydroxyls are also exceptions, and glycerol is the most pronounced exception of the three.

#### RESULTS OBTAINED BY GUY.

The conclusions reached as the result of the investigation by Schmidt were based upon the study of a very few compounds, and these were investigated at only a few temperatures. This earlier work showed, however, that glycerol is such an interesting and important solvent that it seemed desirable to study solutions of a much larger number of salts in it, and to study these over a much larger range in temperature. The work of Dr. Guy was undertaken for this purpose. The temperature range in this work was 25° to 75°, and the salts investigated were potassium nitrate, potassium chloride, potassium bromide; sodium chloride, bromide, iodide, and nitrate; ammonium chloride, bromide, and nitrate; barium chloride, bromide, and nitrate; calcium bromide, strontium bromide and nitrate, and cobalt chloride and bromide.

Potassium chloride, sodium nitrate, ammonium bromide, and strontium chloride were studied also in mixtures of glycerol with water and the alcohols.

The viscosities and fluidities of solutions of all of the above-named salts in glycerol were determined at 25°, 35°, and 45°, and of a number of them at 55°, 65°, and 75°.

The viscosities and fluidities of solutions of a number of these salts were determined in mixtures of glycerol and water, glycerol and ethyl alcohol, and glycerol and methyl alcohol.

In no other solvents is there such a marked change in conductivity with change in temperature, as in glycerol. This change in conductivity with rise in temperature may be due to either of the following causes: A change in the dissociation with rise in temperature, or a change in the velocities of the ions as the temperature is varied. That the temperature coefficients of dissociation, over the above range in temperature, is small is shown by abundant evidence. The main factor, therefore, increasing the conductivity with rise in temperature, is an increase in the velocity of the ions. This may be due to a diminution in the viscosity of the solvent with rise in temperature, or to a breaking down of complex solvates around the ions. We know that the viscosity decreases rapidly with rise in temperature, but we also have evidence that there is solvation in glycerol as a solvent, or the formation of glycerolates by the dissolved substances.

The temperature coefficients of conductivity in glycerol are greater at high than at low dilution. Jones<sup>1</sup> has pointed out that this would be expected from the solvate theory for aqueous solutions, and the same conclusion holds for glycerol as a solvent. The more dilute the solution the more complex the solvate; the more complex the solvate the greater the change in the complexity with rise in temperature. This fact would indicate that glycerolates exist in solutions in glycerol as the solvent.

<sup>1</sup>Carnegie Institution of Washington Publication No. 80.

It was further observed that salts of calcium, strontium, and barium have larger temperature coefficients of conductivity than those of sodium, potassium, and ammonium. The former are very strongly hydrated, while the latter are only slightly hydrated. It is not at all surprising to find that the former combine with far more glycerol than the latter. It should also be noted that salts which have approximately the same hydrating power show temperature coefficients of conductivity in glycerol of the same order of magnitude. The same facts that came out between 25 per cent and 45 per cent manifest themselves also over the higher temperature range, 55° to 75°. The conductivities in the mixed solvents do not follow the law of averages, but are always less, as is shown by the deviation of the curves from a straight line. This has been explained by the work of Jones and Lindsay and of Jones and Murray.<sup>1</sup> Each solvent diminishes the association of the other.

An interesting observation was made in the case of sodium nitrate and potassium chloride. These salts are only slightly soluble in alcohol, and yet their conductivities in mixtures of alcohol and glycerol are strikingly analogous to those of a salt like ammonium bromide, which is soluble in both solvents. This would indicate that the deviation from this law of averages in these cases was due primarily to a change in the association of the glycerol. Study was made of the viscosities of tenth-normal solutions of all of the salts whose conductivities were measured. In most cases the viscosity of the solution was greater than that of the solvent, ammonium bromide being an exception. The temperature coefficients of fluidity are somewhat larger than those of conductivity. This would be expected, since rise in temperature diminishes the dissociation. This would diminish the conductivity and partly affect the increase in conductivity due to increase in fluidity.

Solutions of ternary electrolytes have much greater viscosity than solutions of binary. Those salts whose solutions have the greatest viscosity are the most solvated or combine with the largest amounts of the solvent. This may be due to the fact that ternary electrolytes yield more ions in solution than binary, and there being more surface to the ions than to the molecule from which they came, the surface, and consequently the surface friction, would be thus increased. Viscosity is an expression of the surface friction. Probably the small atomic volumes of calcium, strontium, barium, and cobalt also have something to do with the large viscosities of solutions of their salts in glycerol.

It may be said, in general, that the curves representing the change in conductivity of salts in glycerol with temperature and those representing the change in fluidity are very similar, conductivity and fluidity running almost parallel from 25° to 75°.

Analogous relations were found to hold in the mixed solvents, the viscosity of the solution being nearly always greater than that of the pure mixed solvent.

The viscosity of glycerol changes very rapidly with temperature. It is obvious that there is a close connection between the viscosity of a solvent and the velocity of the reaction in that solvent. The ions must first come near together before they can react chemically. The frequency of their approach is conditioned by the viscosity of the solvent. We propose to study reaction velocities in glycerol from the standpoint of the relation between reaction velocities and viscosity, and the change

<sup>1</sup>Carnegie Institution of Washington Publication No. 80.

in both with temperature. Dr. Guy found in this work that certain salts actually lower the viscosity of glycerol when they are dissolved in it.

Jones and Veazey<sup>1</sup> had pointed out that it is only salts of potassium, rubidium, and cæsium which lower the viscosity of water, and they explained this fact as due to the large atomic volumes of these elements.

Salts of rubidium were found to lower the viscosity of glycerol, and the same explanation was offered of this phenomenon that had been offered by Jones and Veazey to explain the similar phenomenon in water.

Ammonium bromide and iodide were also found to lower the viscosity of glycerol. This is not surprising, since ammonium is so closely analogous in its properties in general to the other elements of the alkali group.

#### RESULTS OBTAINED BY DAVIS.

It was pointed out in discussing the work of Dr. Guy that rubidium and ammonium salts showed negative viscosity coefficients in glycerol. The salts were studied elaborately by Dr. Davis. He worked with ammonium iodide in glycerol at 25°, 35°, and 45°; also at 55°, 65°, and 75°. He studied rubidium chloride, rubidium bromide, rubidium iodide, and rubidium nitrate over the same range in temperature.

In mixtures of glycerol with water, he studied ammonium iodide and rubidium bromide.

He measured the viscosity and fluidity of ammonium iodide, rubidium chloride, bromide, iodide, and nitrate in glycerol from 25° to 75°; also the viscosity and fluidity of ammonium iodide and rubidium bromide in mixtures of glycerol and water from 25° to 45°.

This investigation had had to do chiefly with the viscosity in glycerol, and the lowering of the viscosity of glycerol by certain salts when dissolved in it. The conductivity data obtained confirm the conclusions already reached by Jones and Schmidt and by Guy and Jones.

The viscosities of the solutions of the above-named salts in pure glycerol from 25° to 75° were determined for a range of dilution from normal to one-tenth normal, and were found always to have a smaller viscosity than the solvent. The fluidity and conductivity curves in general run parallel to one another. It was pointed out by Dr. Davis that solutions of rubidium salts in glycerol are examples of salts lowering the viscosity of a solvent to such an extent as to increase appreciably their own conductivity in that solvent.

A comparison of the effect of the chloride, bromide, and iodide of rubidium on the viscosity or fluidity of glycerol shows that the chloride has the least effect, the bromide next, while the iodide has the greatest effect on the viscosity of this solvent. Dr. Davis explains this as due to the molecular volumes of the salts in question, the cation, rubidium, being constant in all three of them. If we divide the molecular weights of the three halogen compounds of rubidium by their densities referred to water as unity, we have  $\text{RbCl}=5.50$ ;  $\text{RbBr}=5.95$ ;  $\text{RbI}=7.02$ . The effects on fluidities are in the same order. At 25° and normal concentration, the fluidity of glycerol is increased 12.2 per cent by rubidium chloride, 18.5 per cent by rubidium bromide, and 26.3 per cent by rubidium iodide.

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<sup>1</sup>Carnegie Institution of Washington Publication No. 80.

It was impossible to prepare a normal solution of rubidium nitrate in glycerol at 20°. A fourth-normal solution, however, produced an effect on the viscosity which was intermediate between that of the bromide and the iodide, which was in keeping with its molecular volume.

The rubidium salts referred to above show negative viscosity coefficients in water. They also show negative viscosity coefficients in mixtures of water and glycerol.

It is a special pleasure to thank the Carnegie Institution of Washington for generous financial aid with which to continue the investigations discussed in this monograph.

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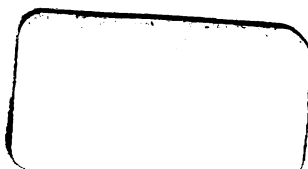




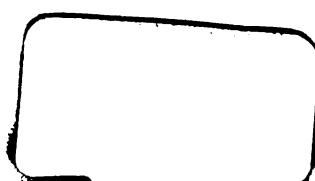


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